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Heo et al.

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(54) **DE-FLUORIDATION PROCESS**
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U.S. Office Action mailed Jul. 25, 2006, from U.S. Appl. No. 10/648,953.

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H01L 21/44 (2006.01)
H01L 21/31 (2006.01)

(Continued)

(52) **U.S. Cl.** **438/597**; 438/437; 438/731;
438/766; 257/E21.235

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(58) **Field of Classification Search** 438/498,
438/731, 739

See application file for complete search history.

(57) **ABSTRACT**

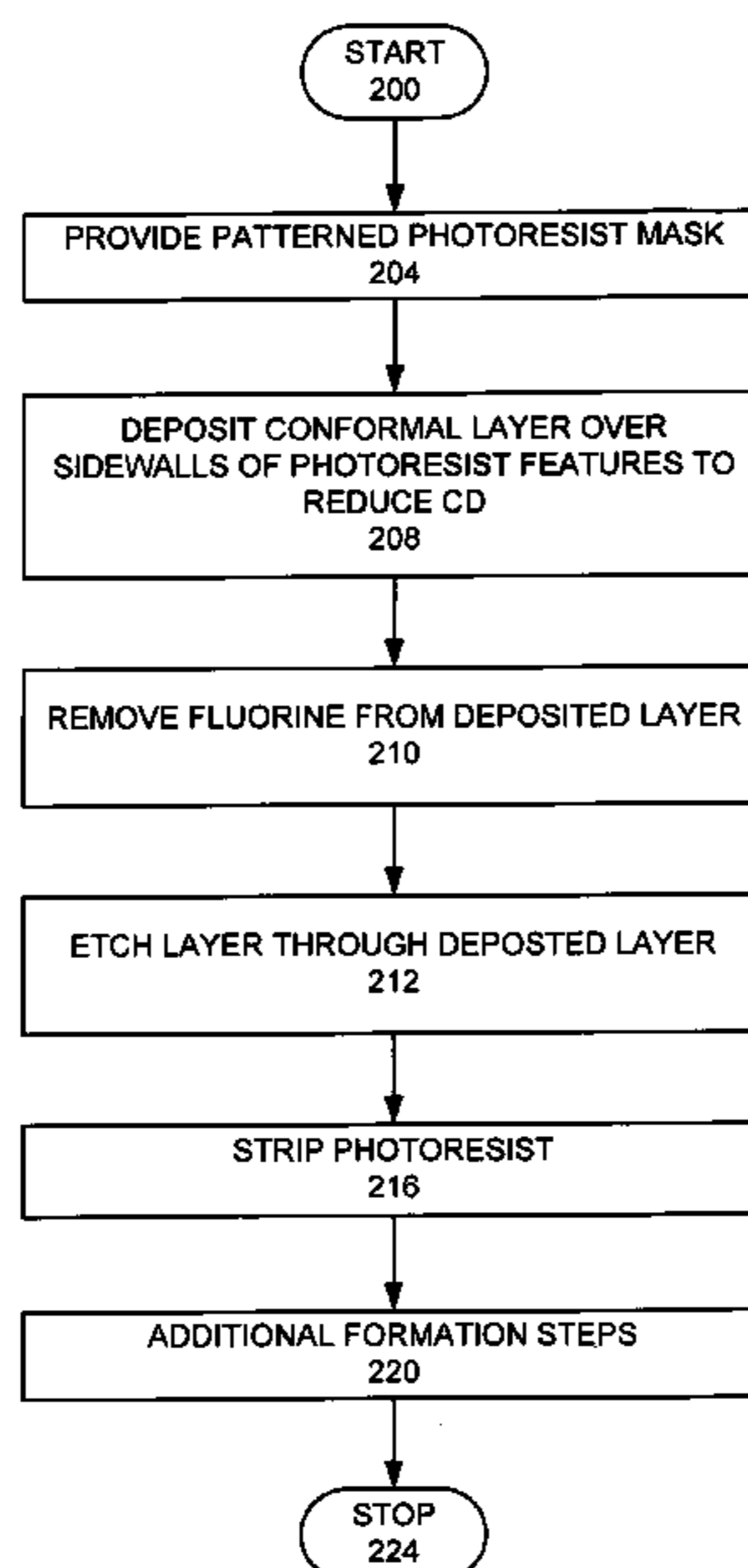
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A feature in a layer is provided. A photoresist layer is formed over the layer. The photoresist layer is patterned to form photoresist features with photoresist sidewalls, where the photoresist features have a first critical dimension. A fluorine-containing conformal layer is deposited over the sidewalls of the photoresist features to reduce the critical dimensions of the photoresist features. Fluorine is removed from the conformal layer, while the remaining conformal layer is left in place. Features are etched into the layer, wherein the layer features have a second critical dimension, which is less than the first critical dimension.

25 Claims, 19 Drawing Sheets



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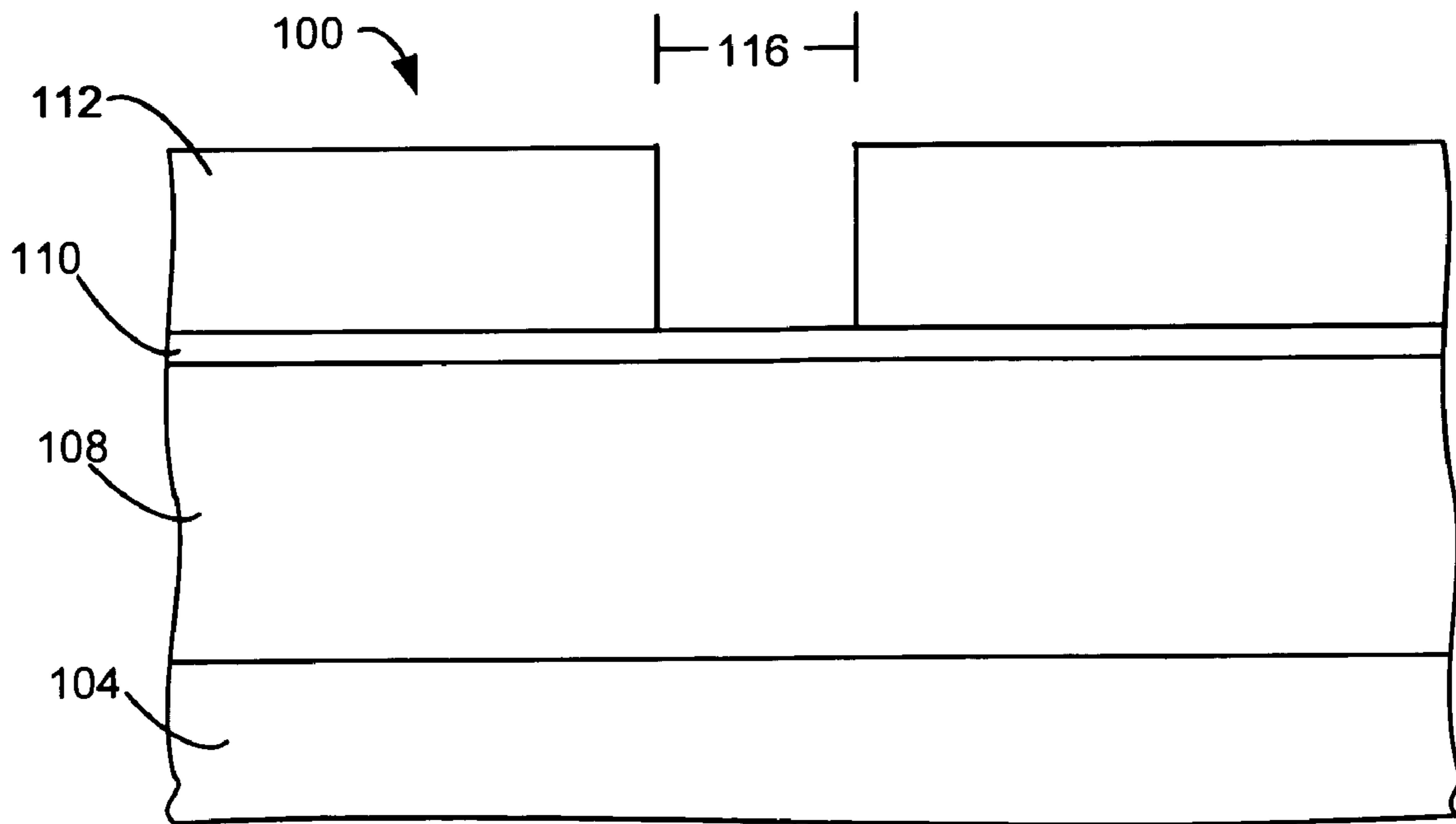


FIG. 1A (PRIOR ART)

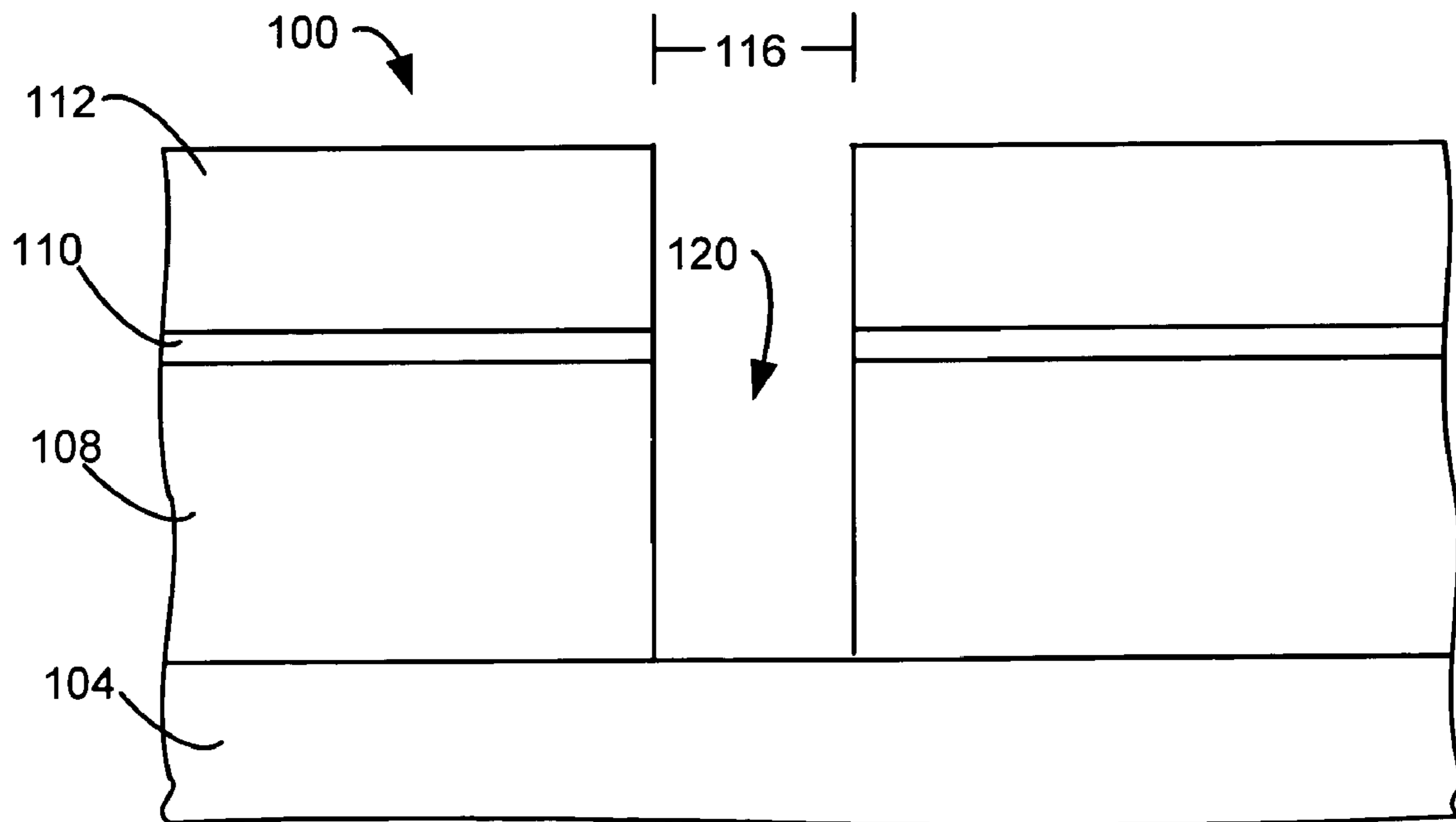


FIG. 1B (PRIOR ART)

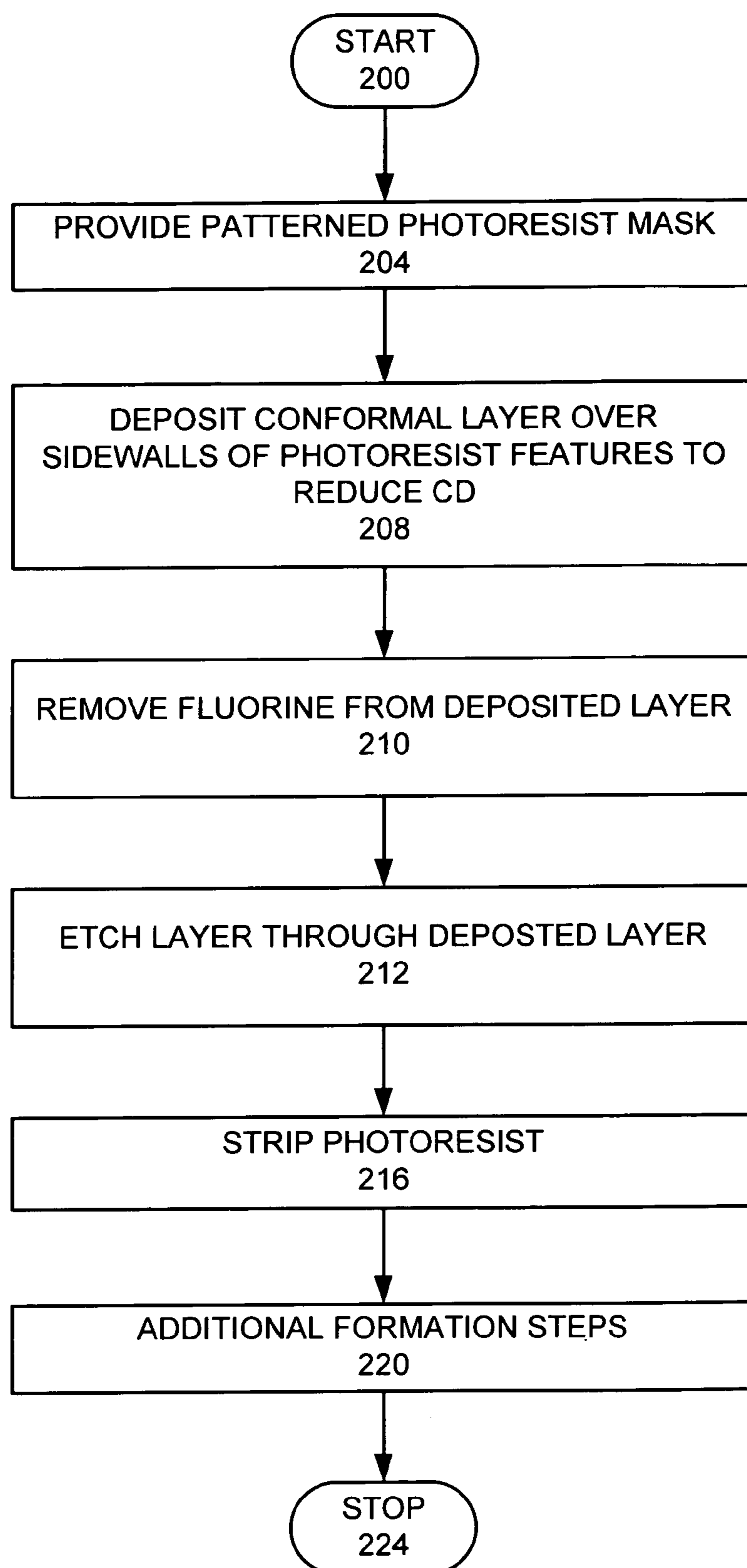


FIG. 2

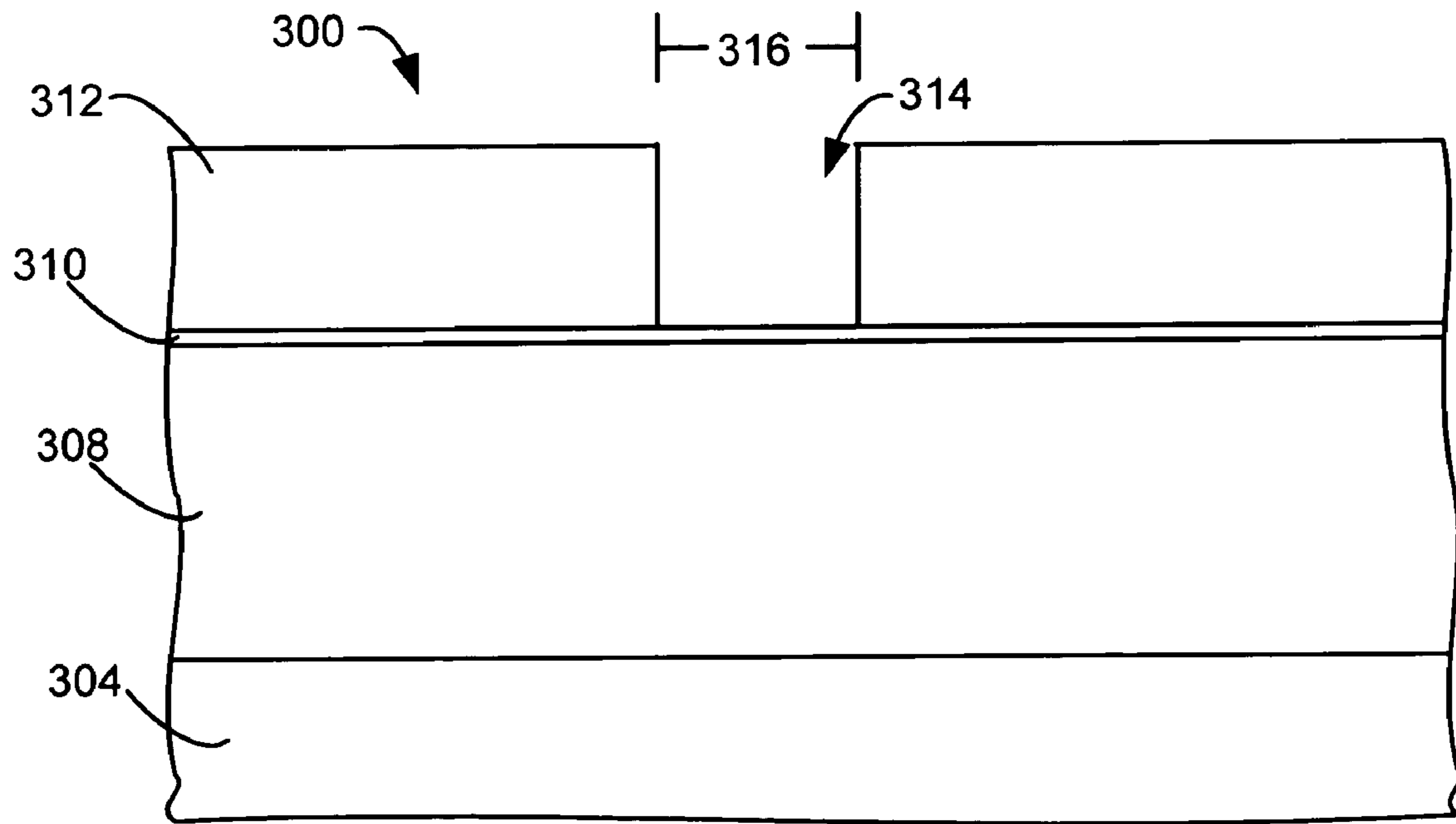


FIG. 3A

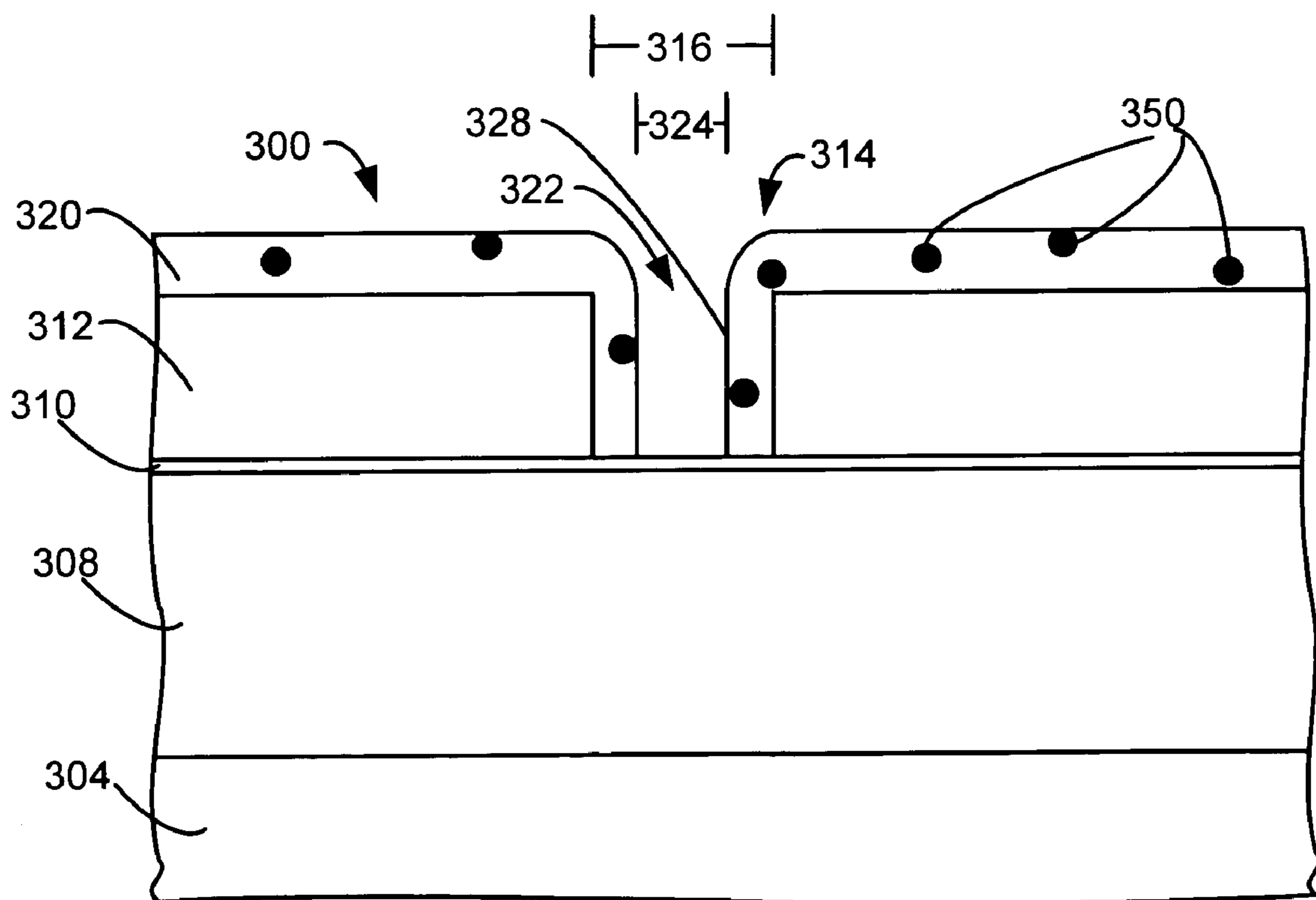


FIG. 3B

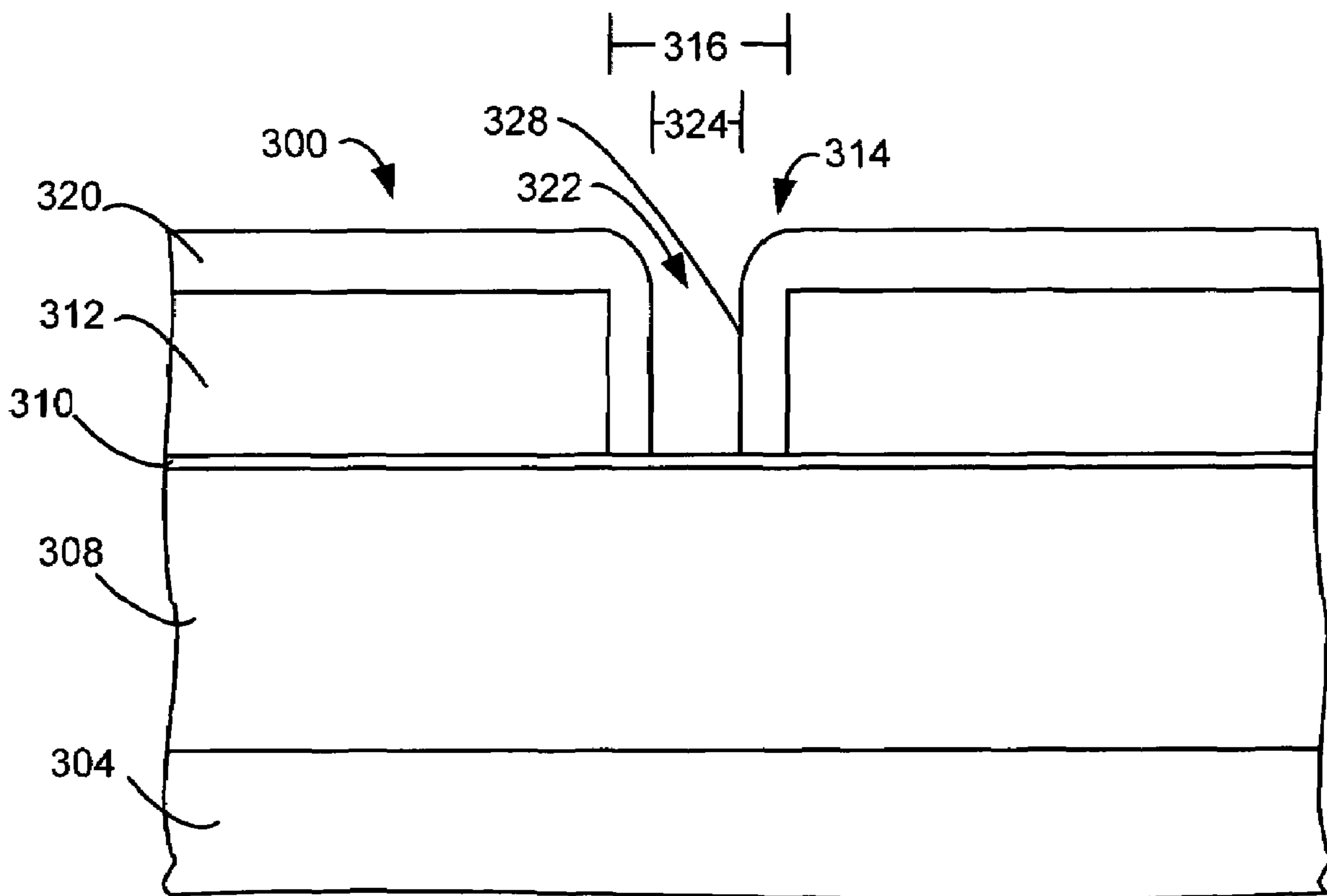


FIG. 3C

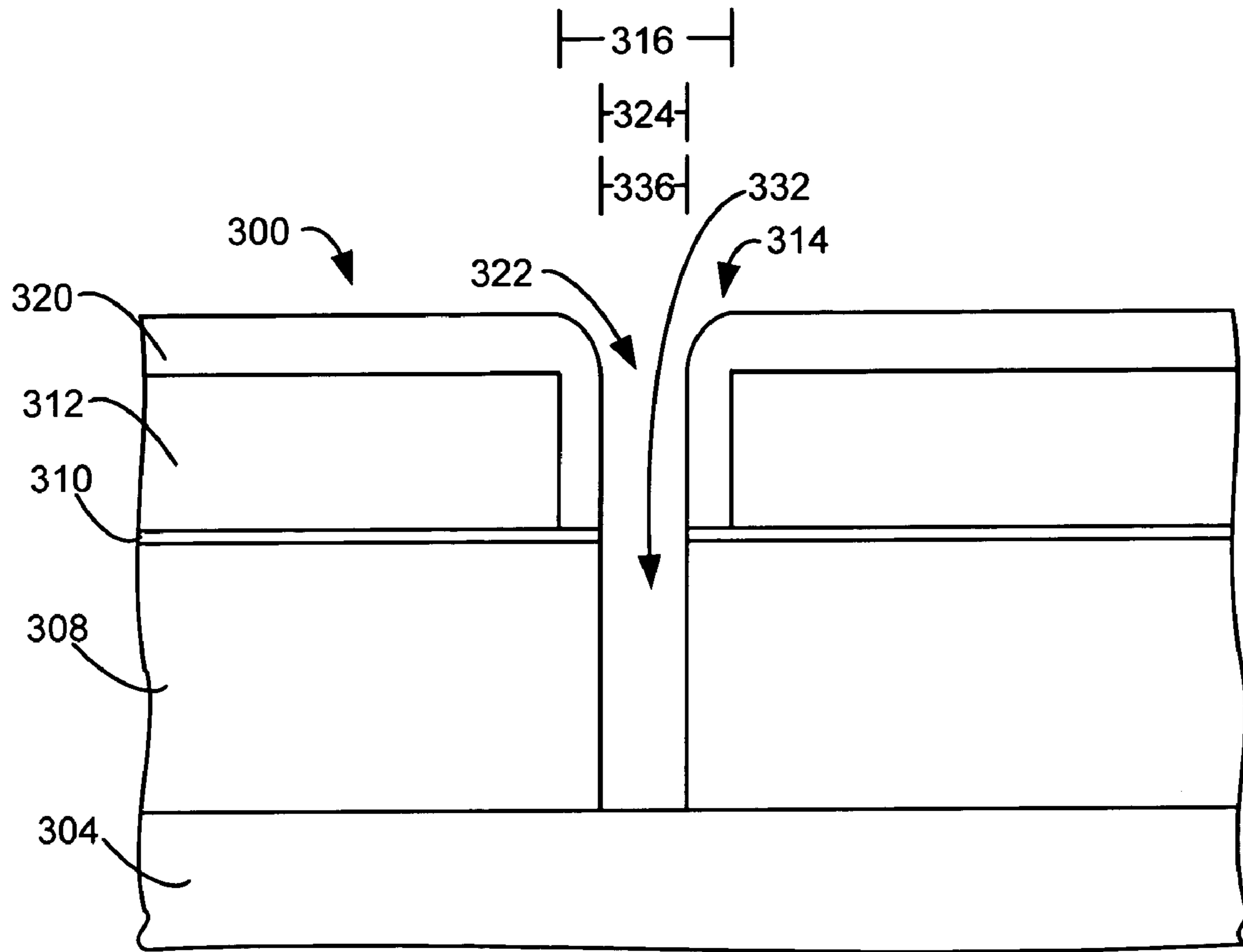


FIG. 3D

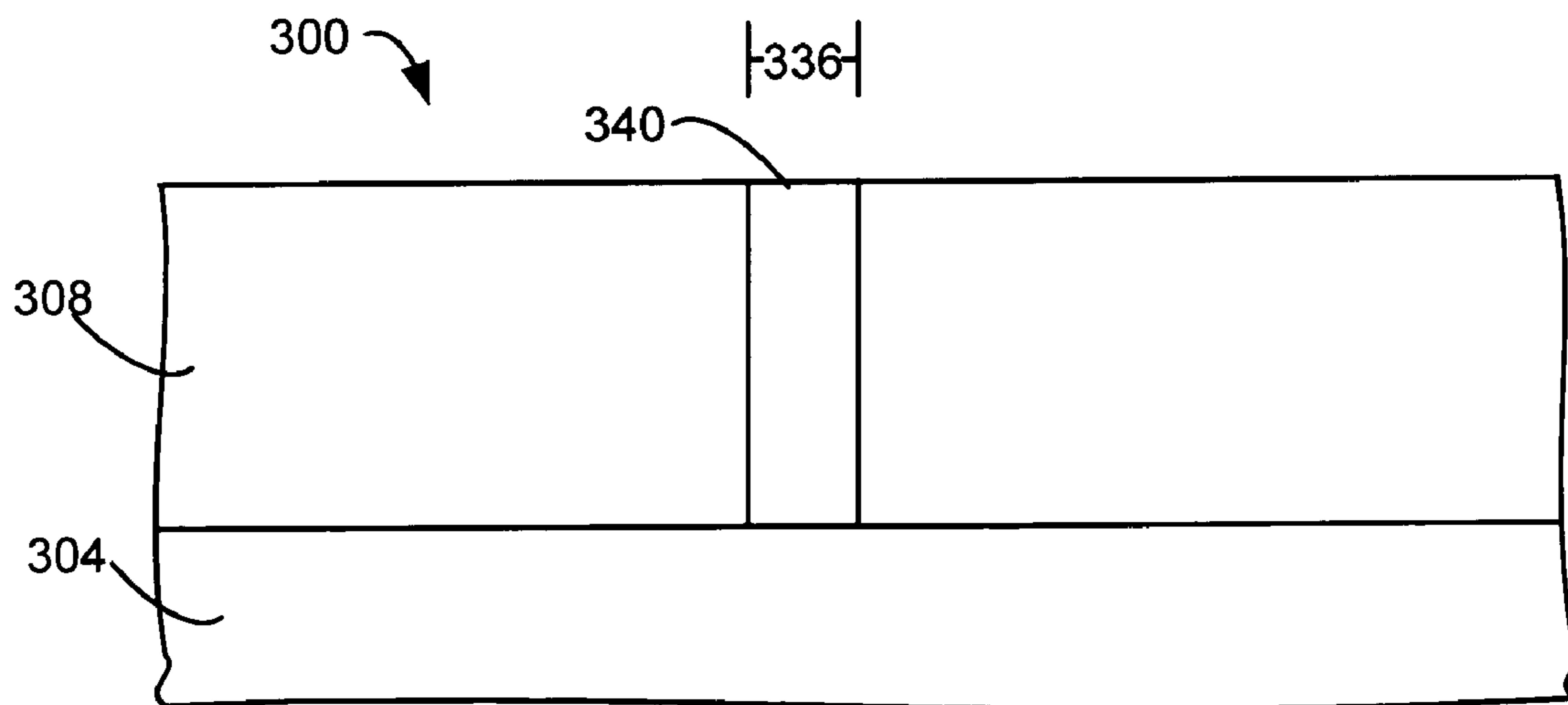


FIG. 3E

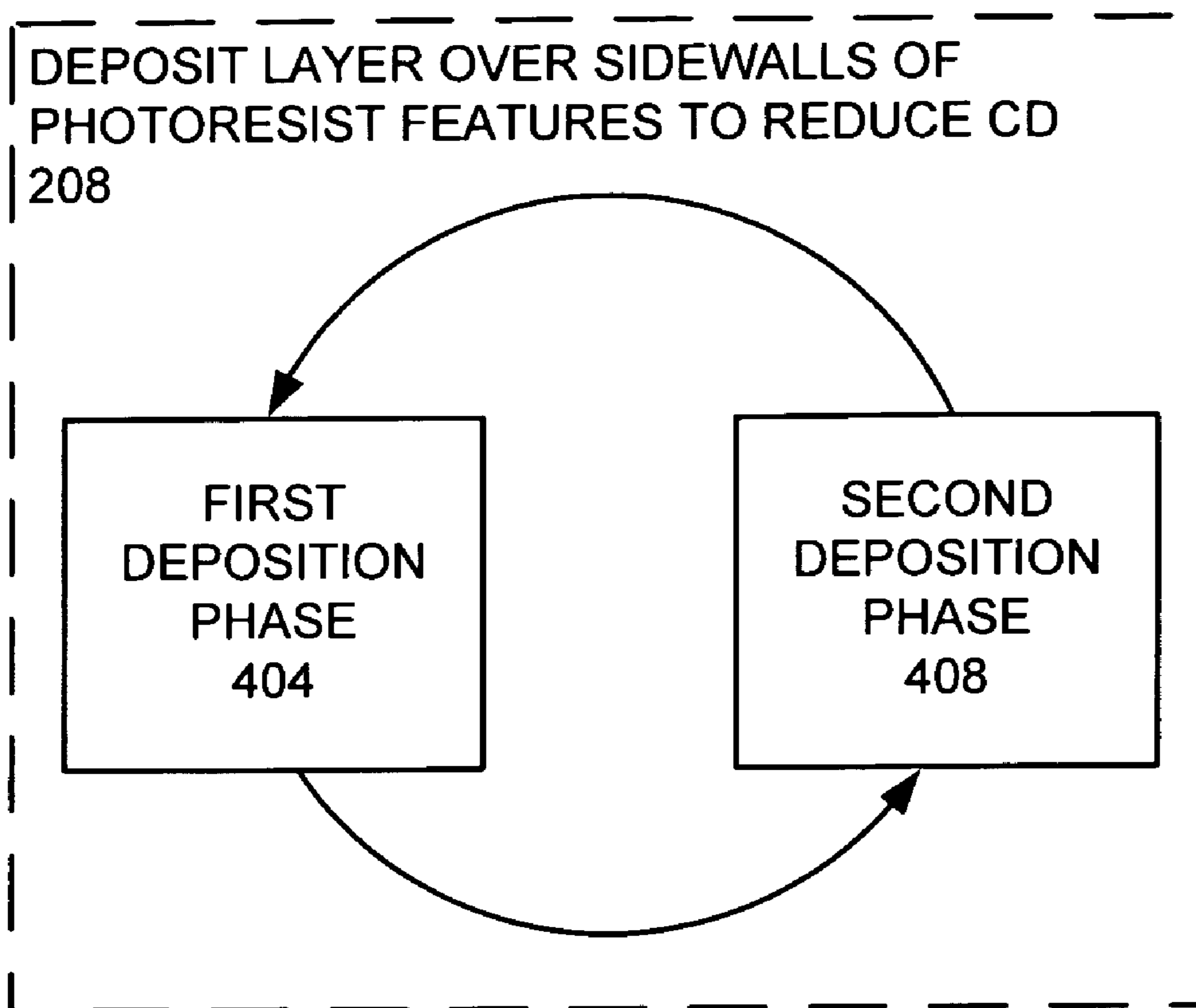


FIG. 4

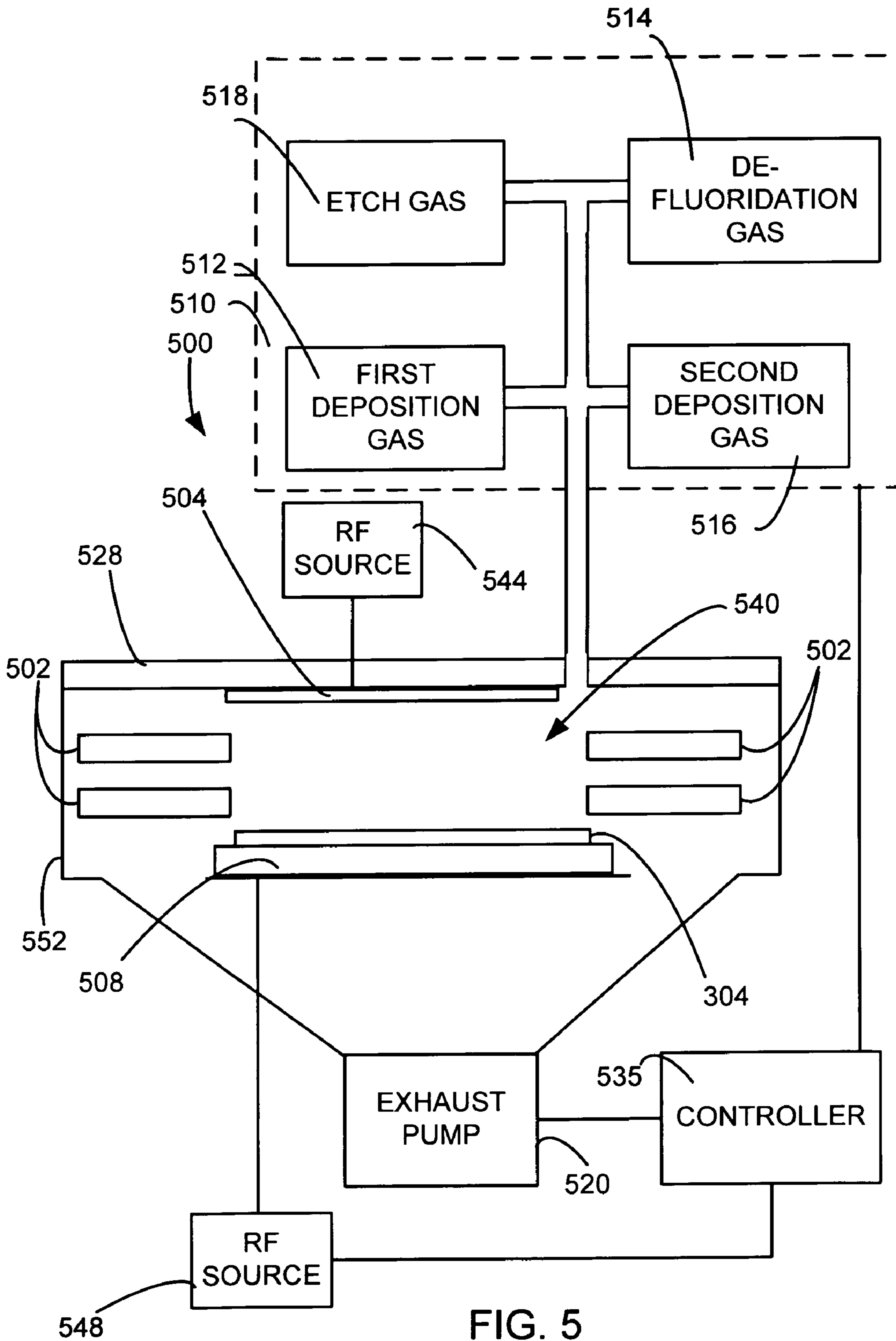


FIG. 5

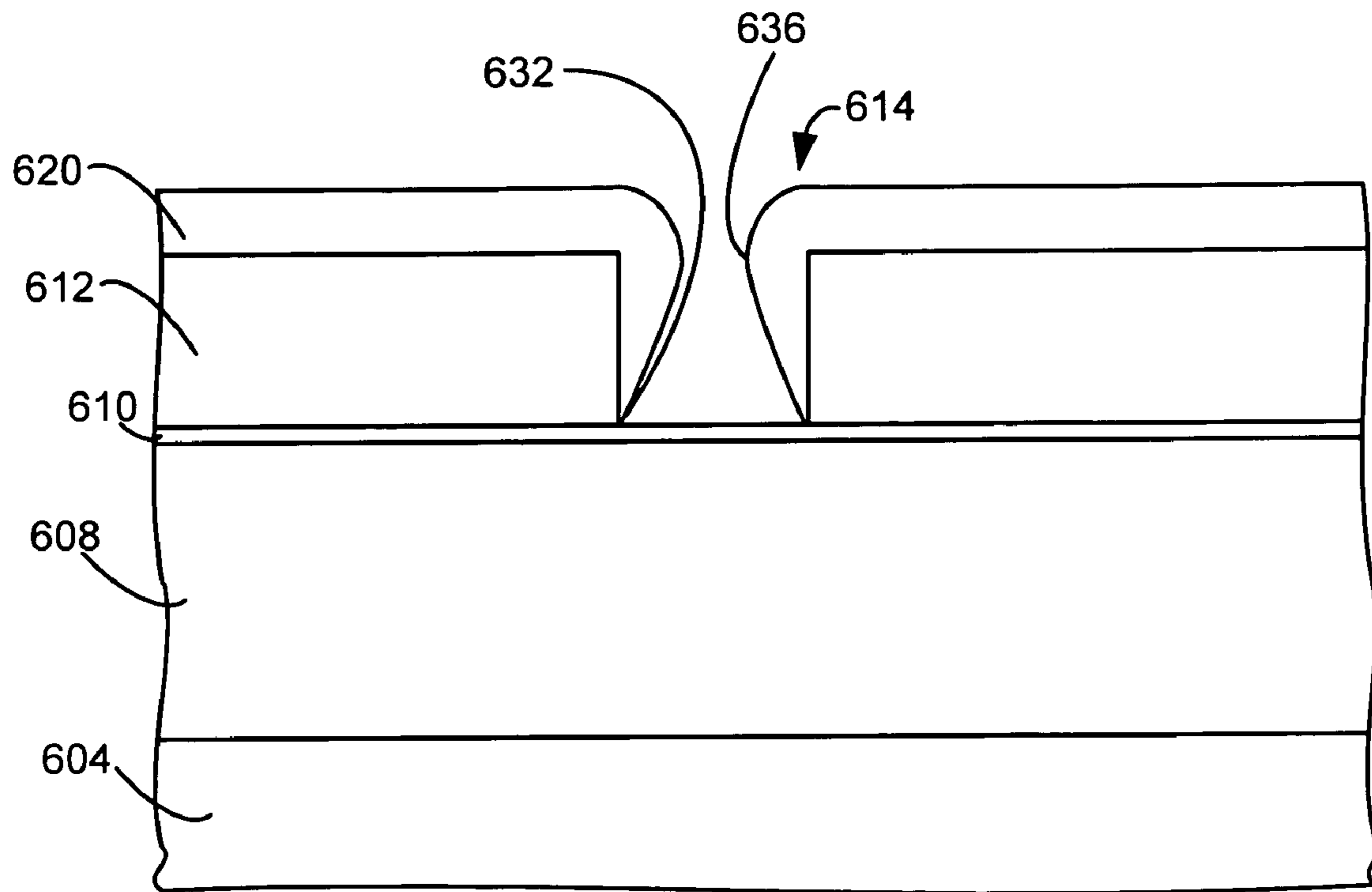


FIG. 6

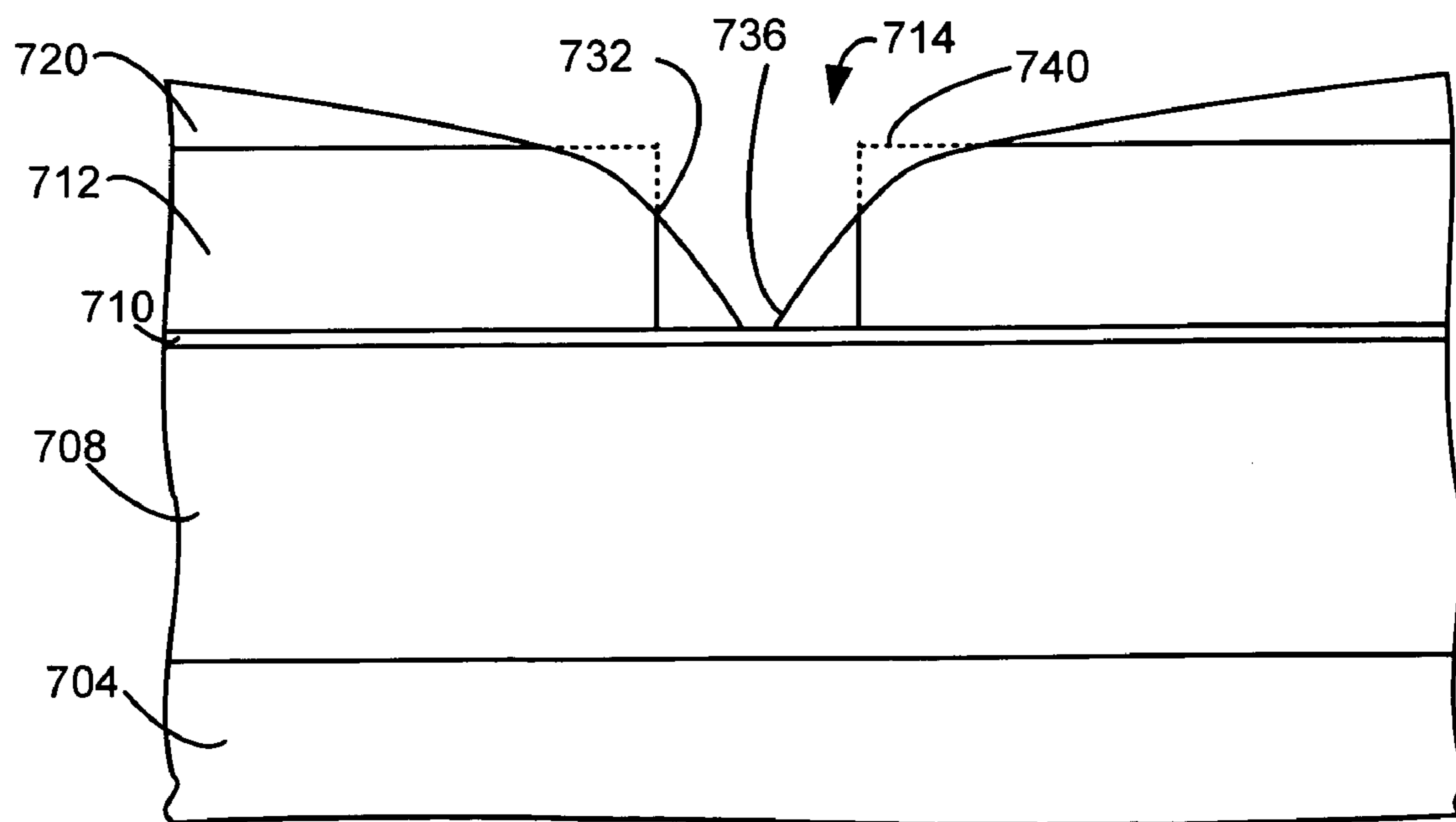
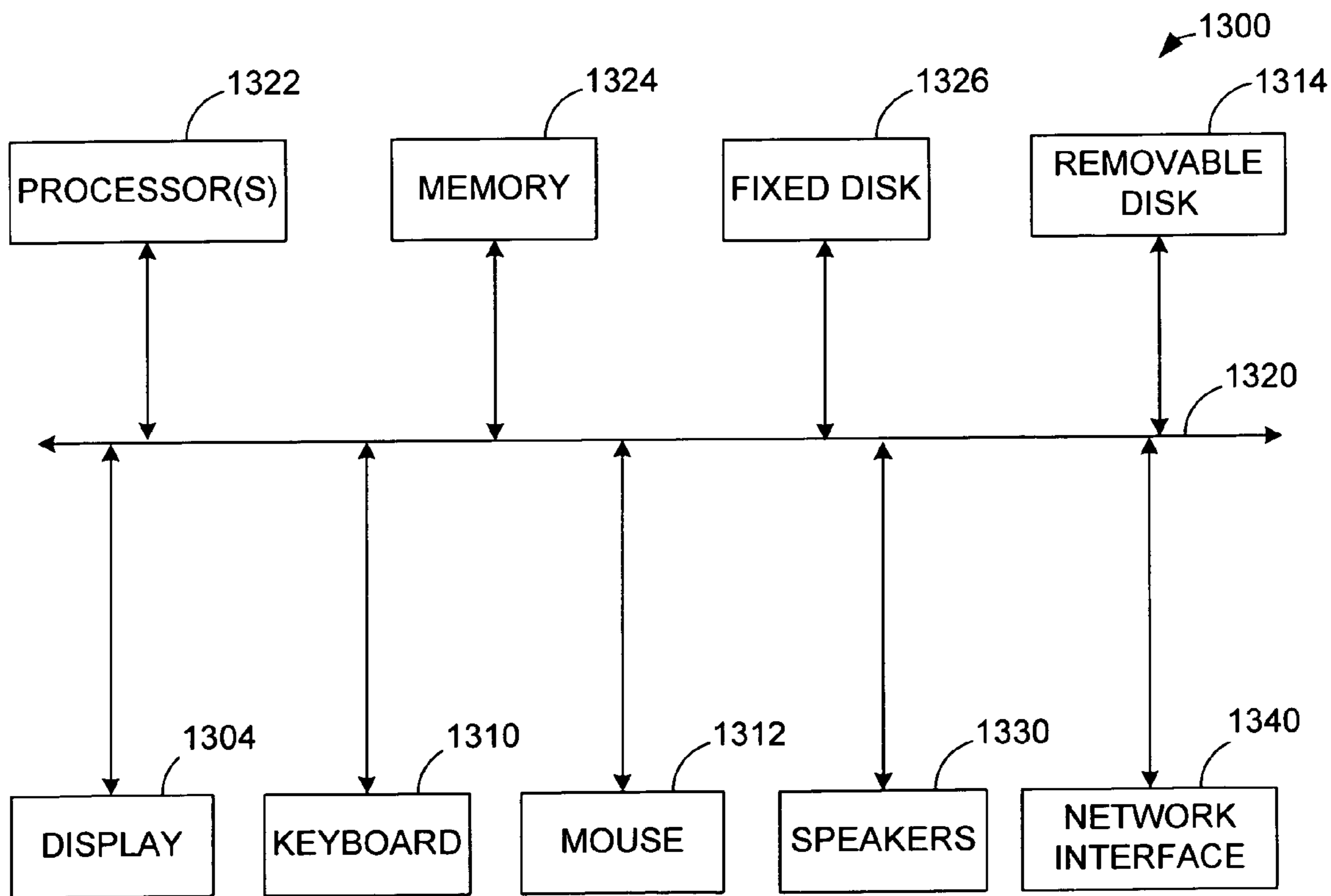
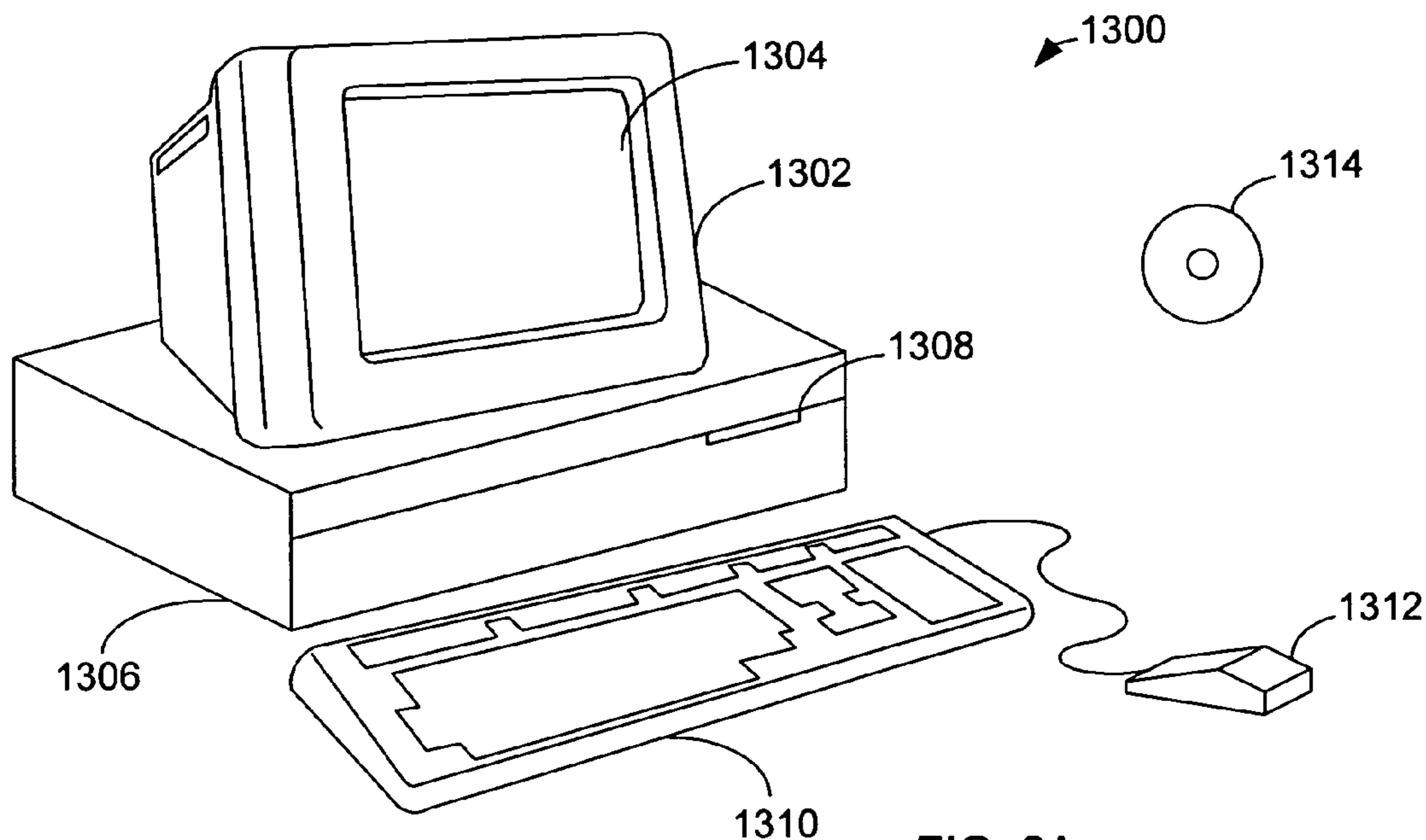


FIG. 7



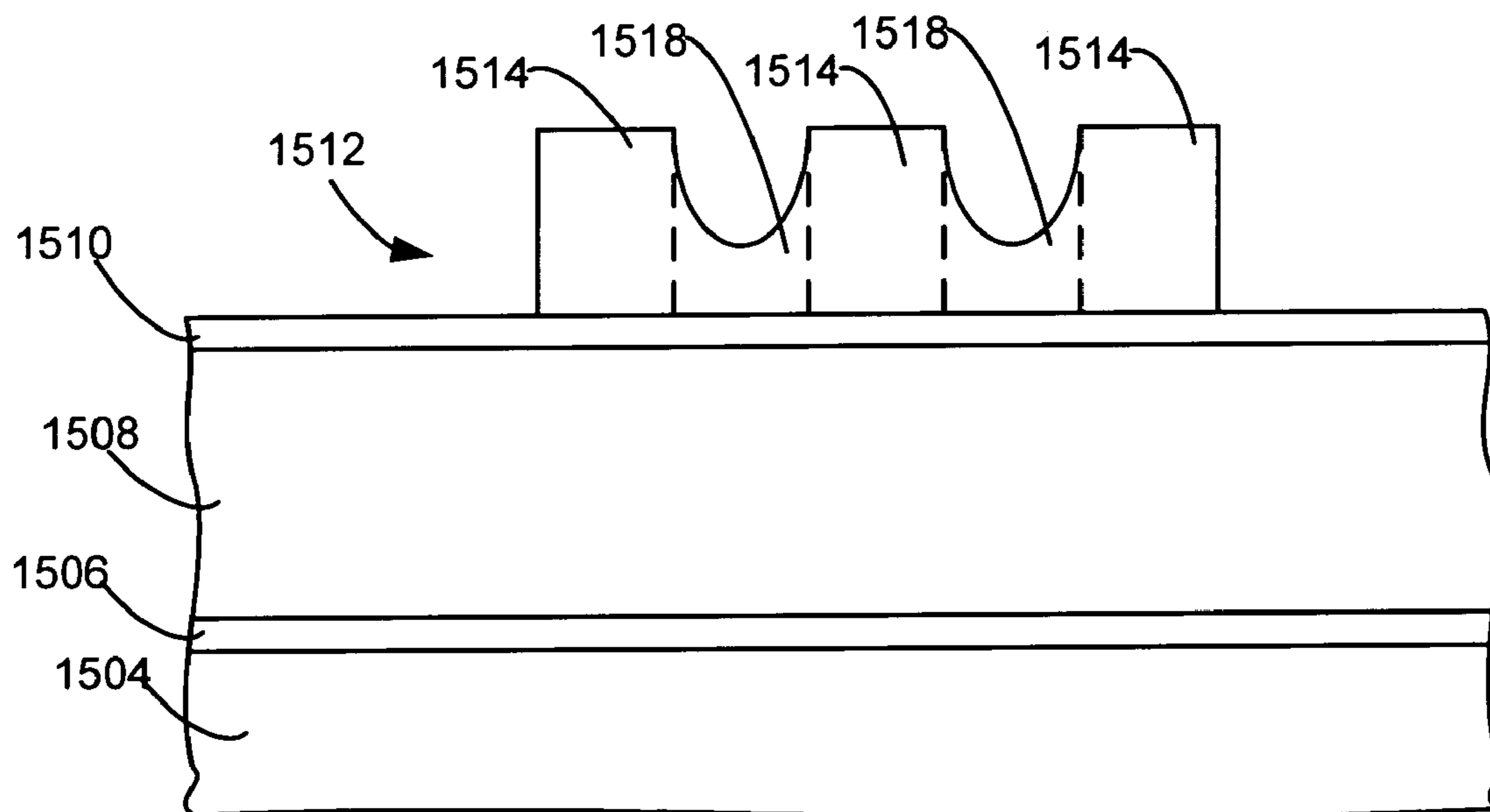


FIG. 9 A (PRIOR ART)

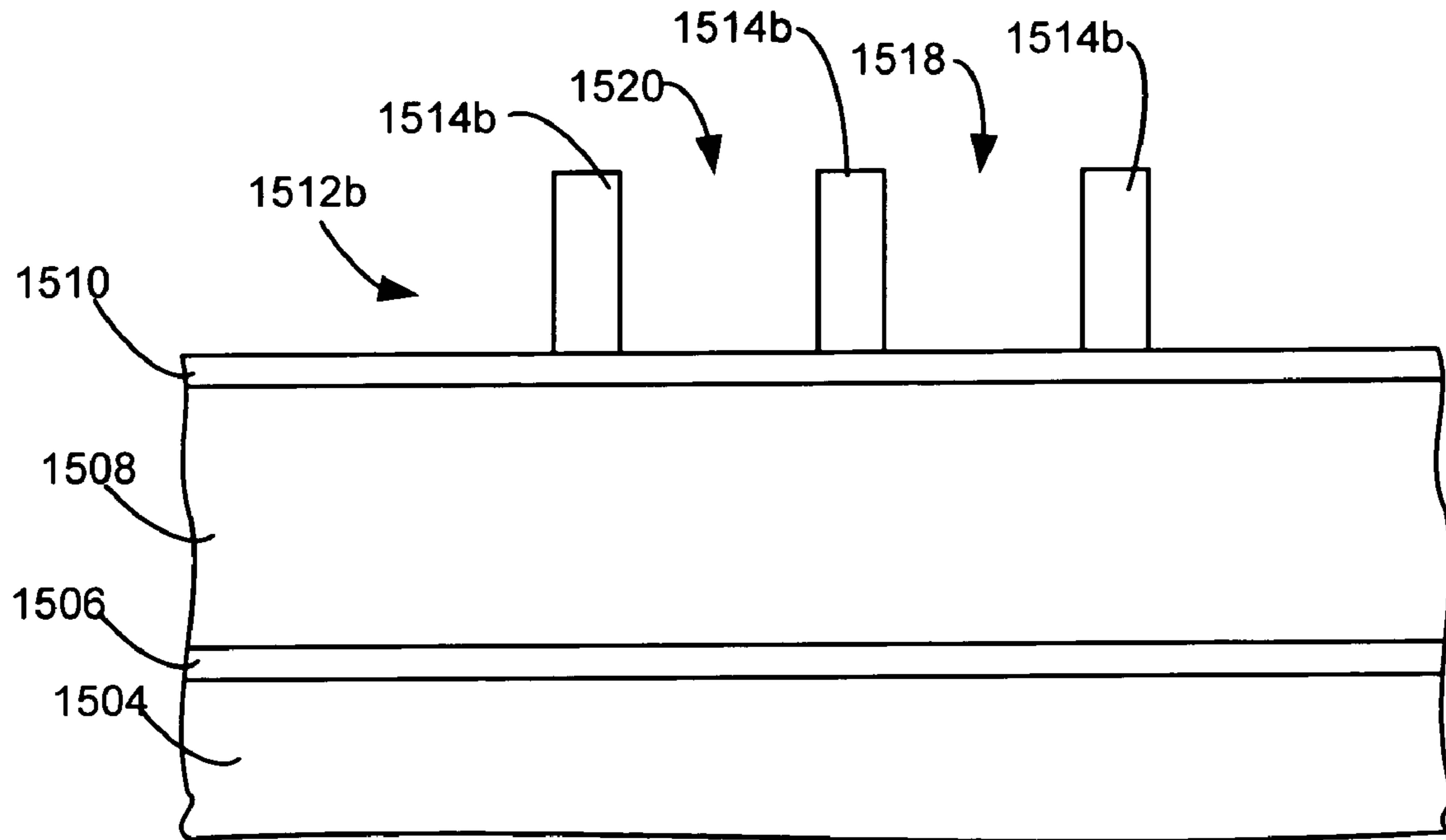


FIG. 9 B (PRIOR ART)

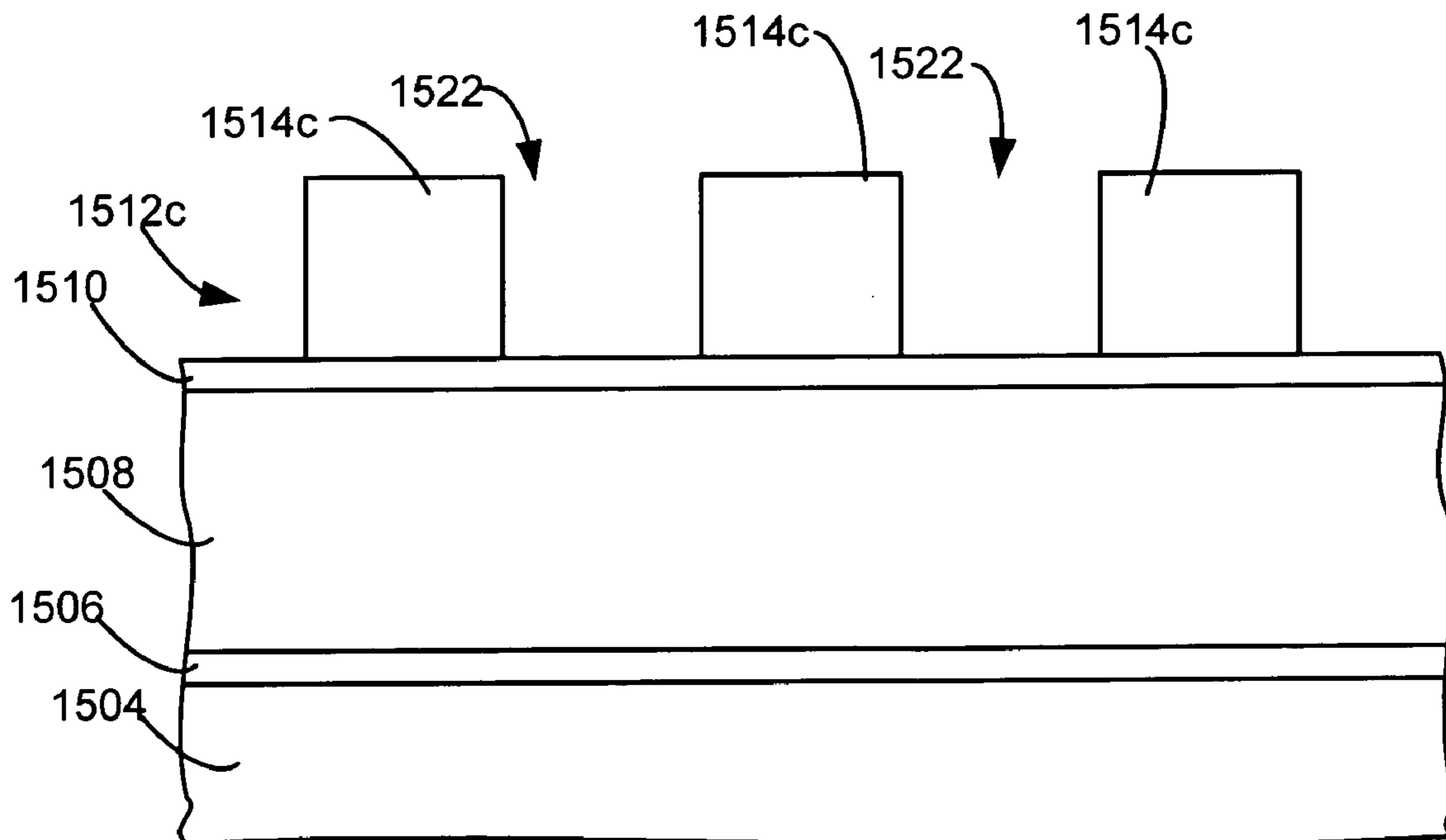


FIG. 9 C (PRIOR ART)

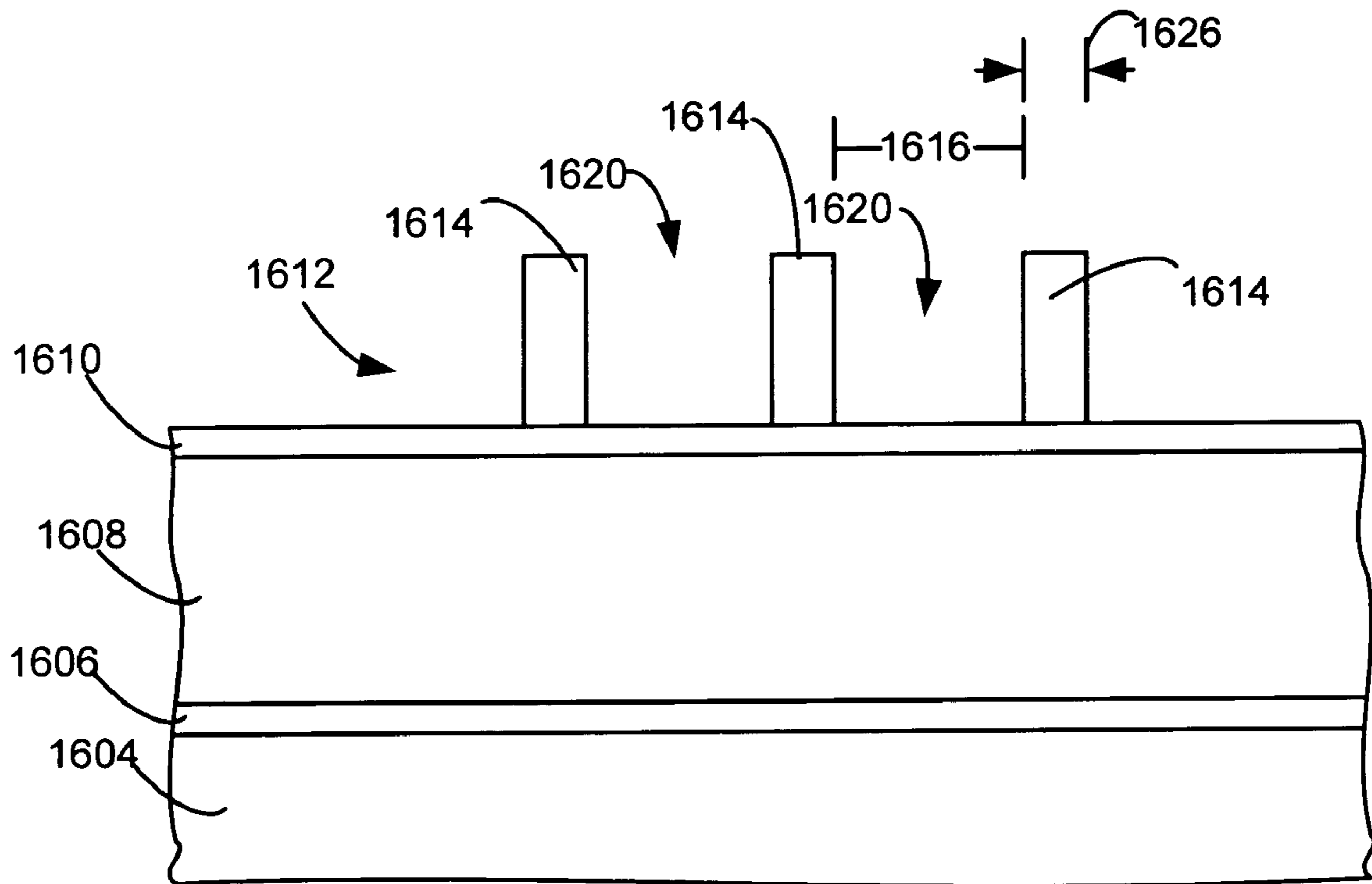


FIG. 10A

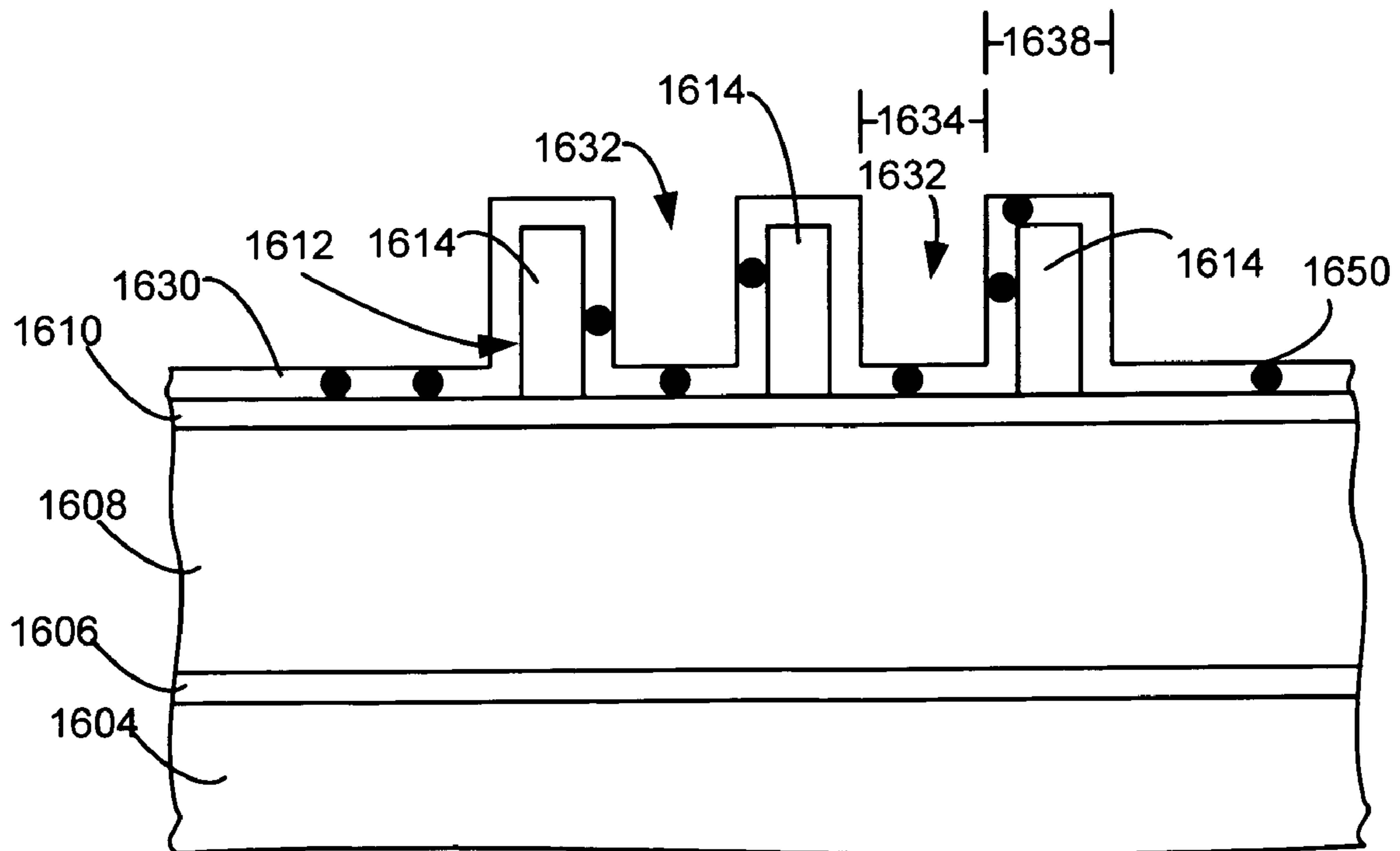


FIG. 10B

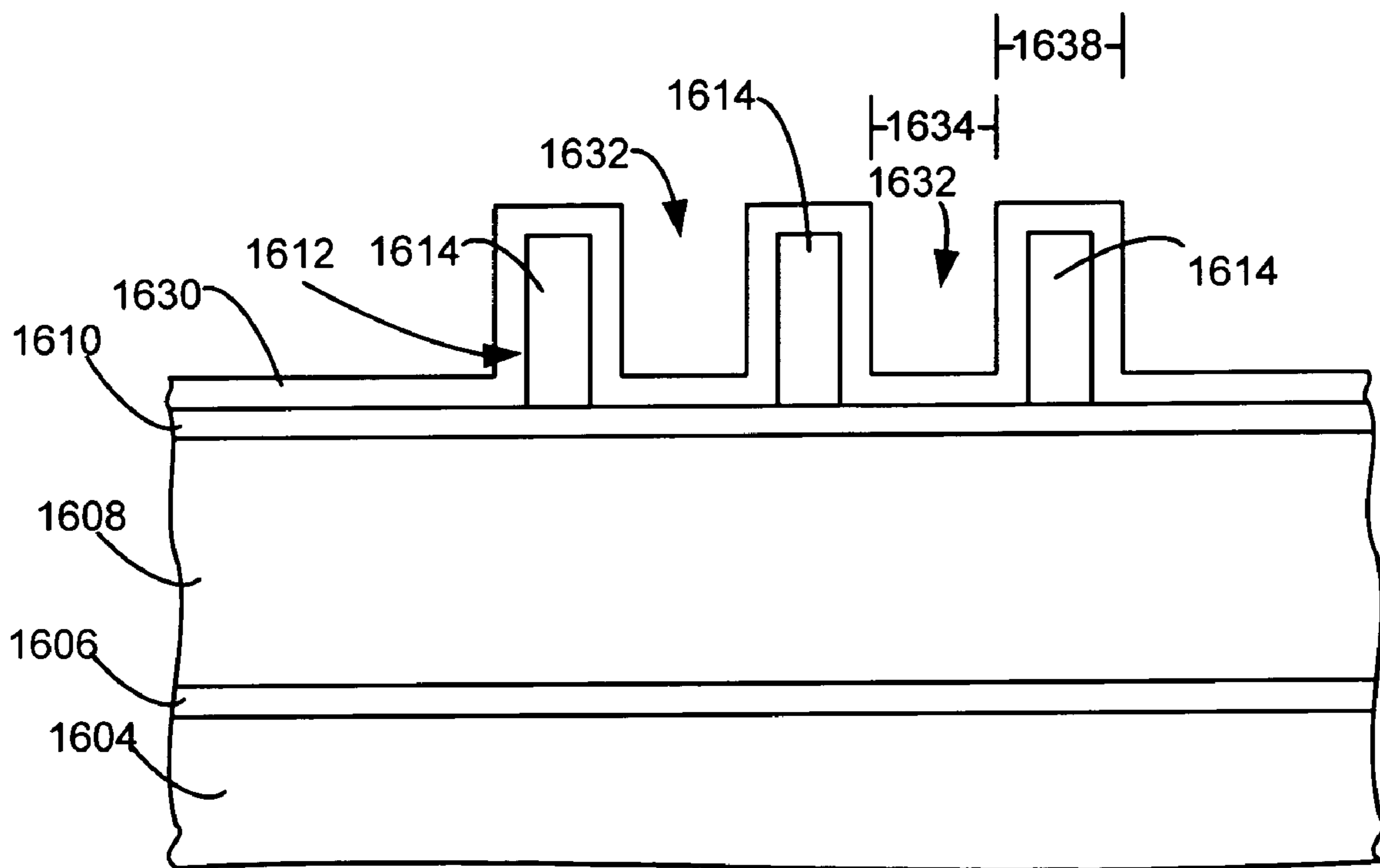


FIG. 10C

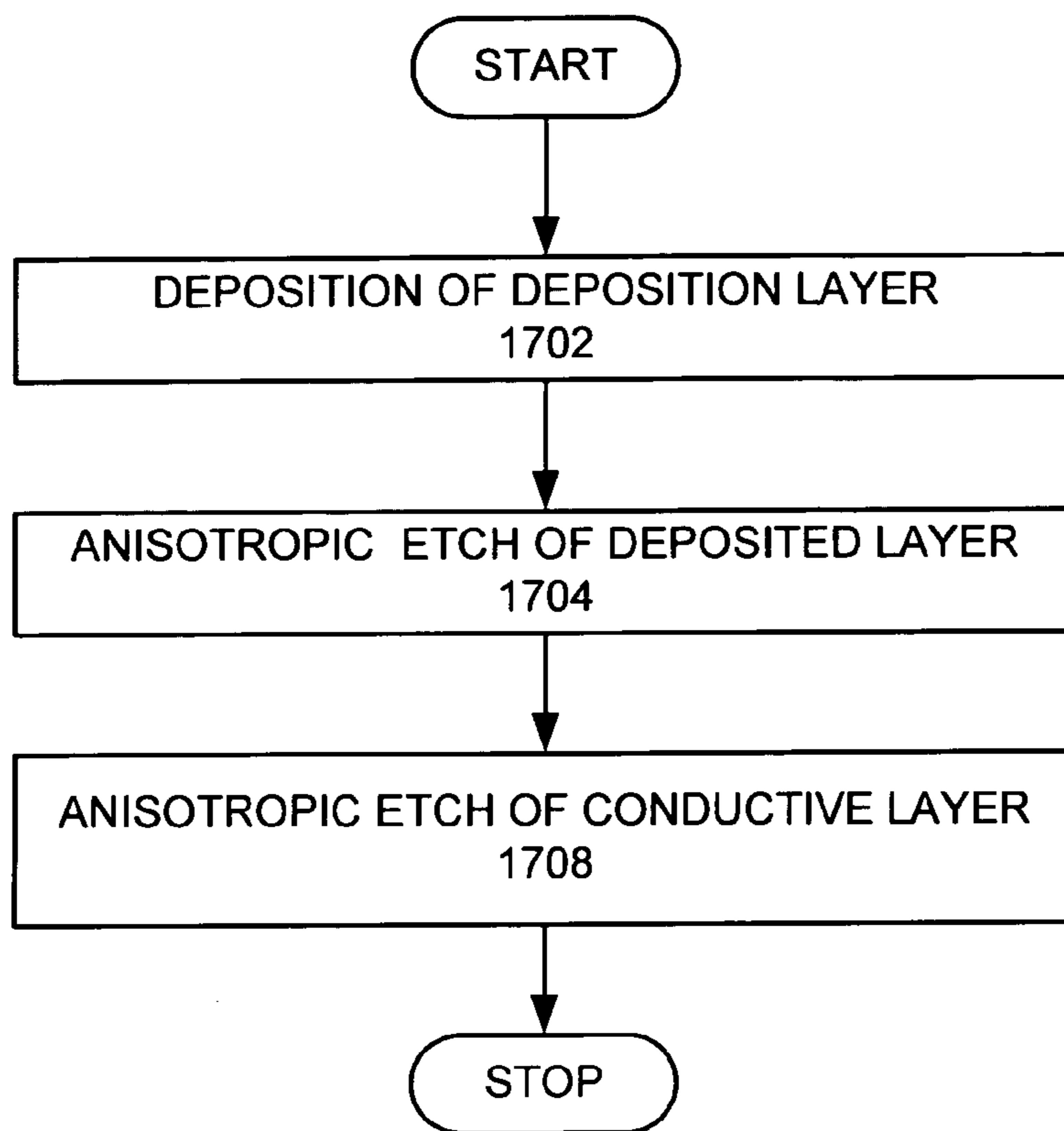


FIG. 11

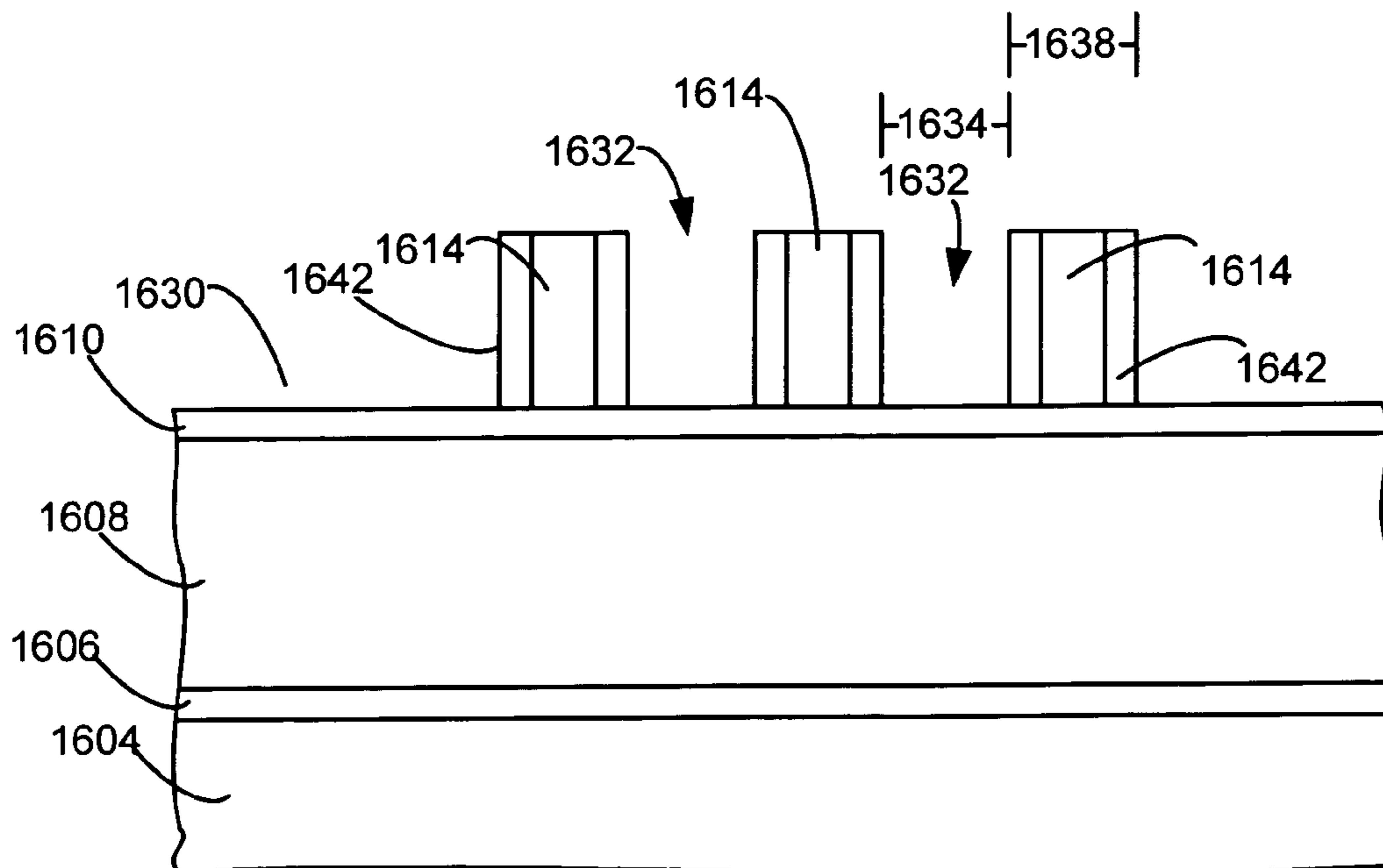


FIG. 10D

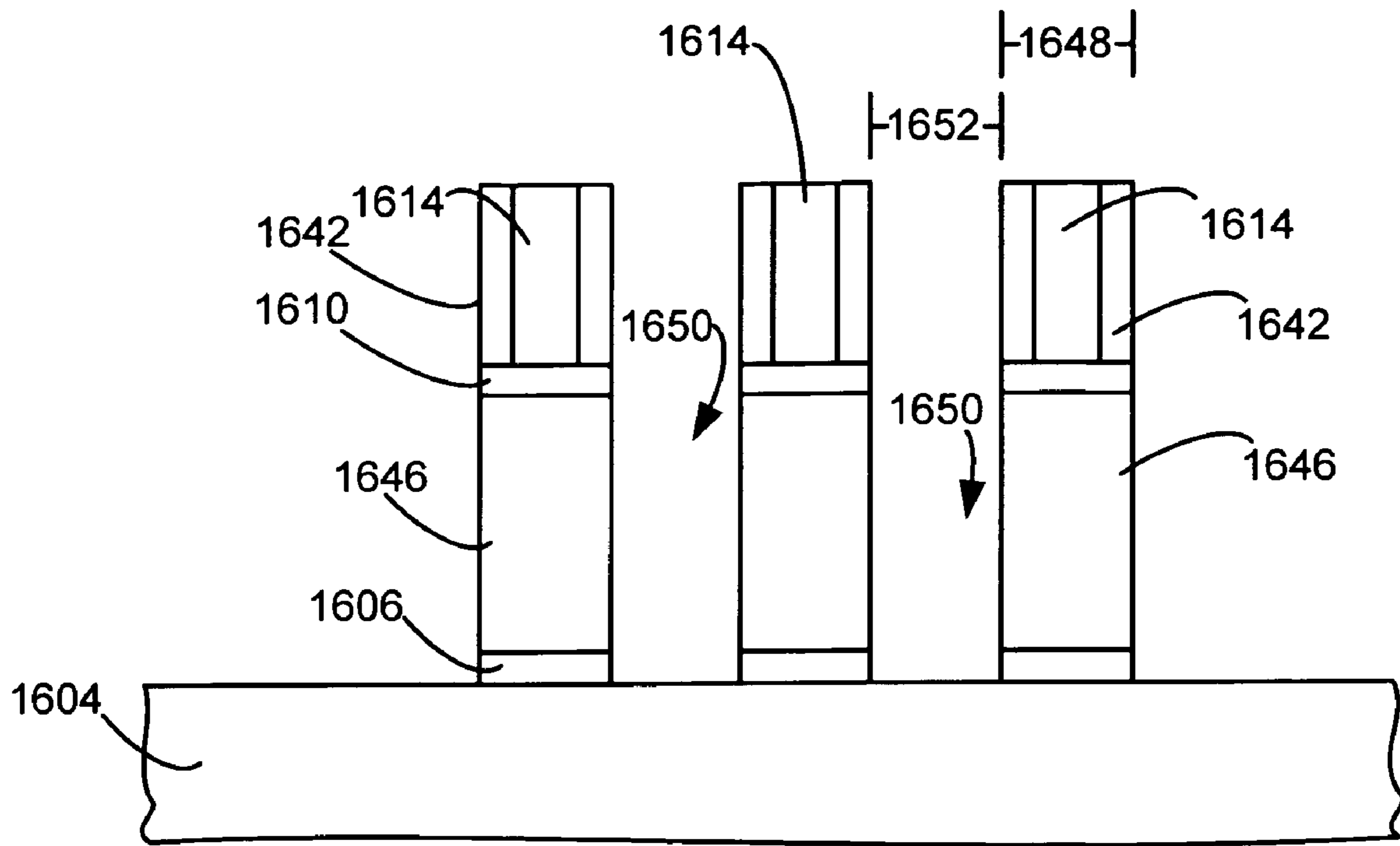


FIG. 10E

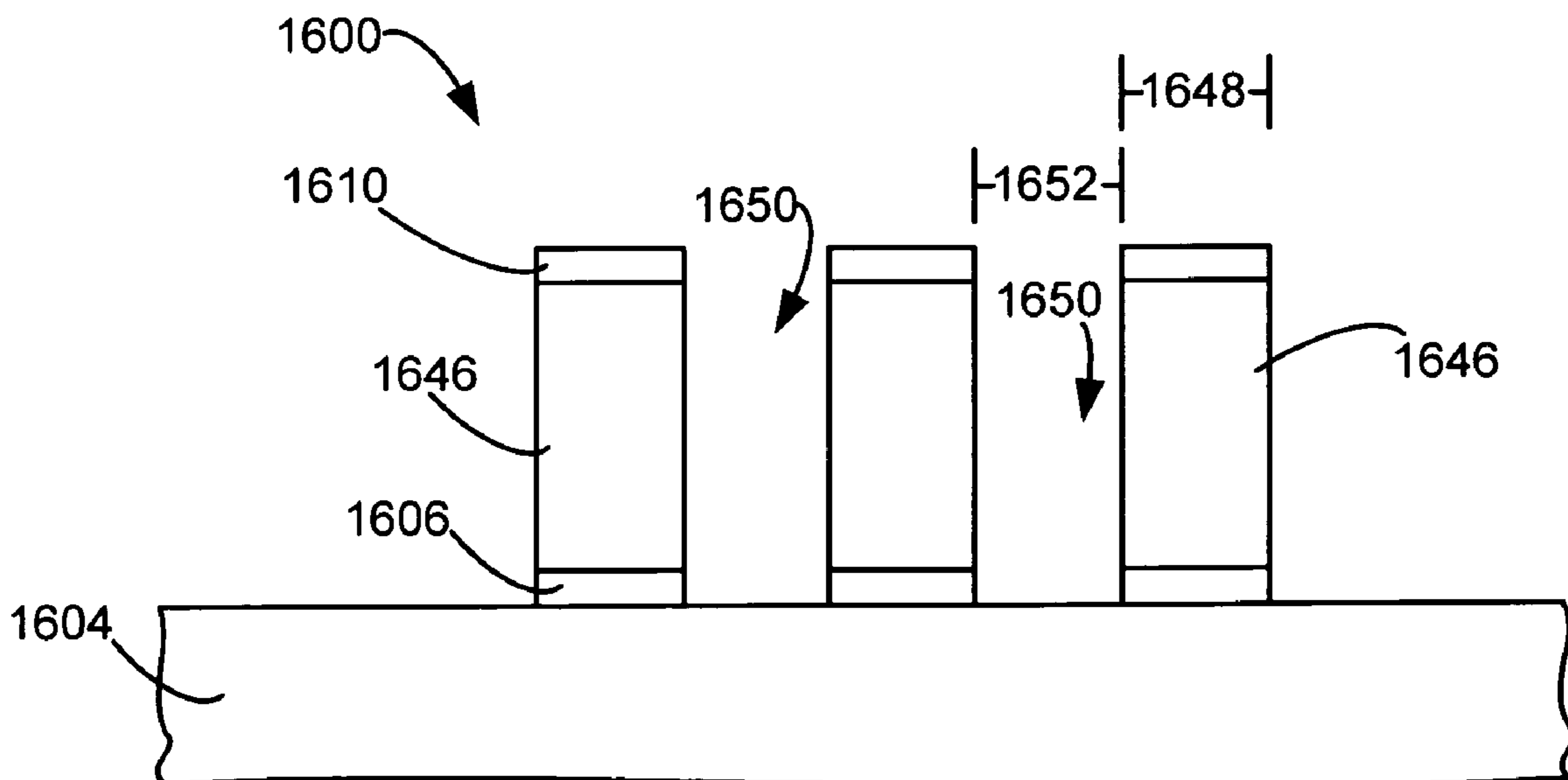


FIG. 10F

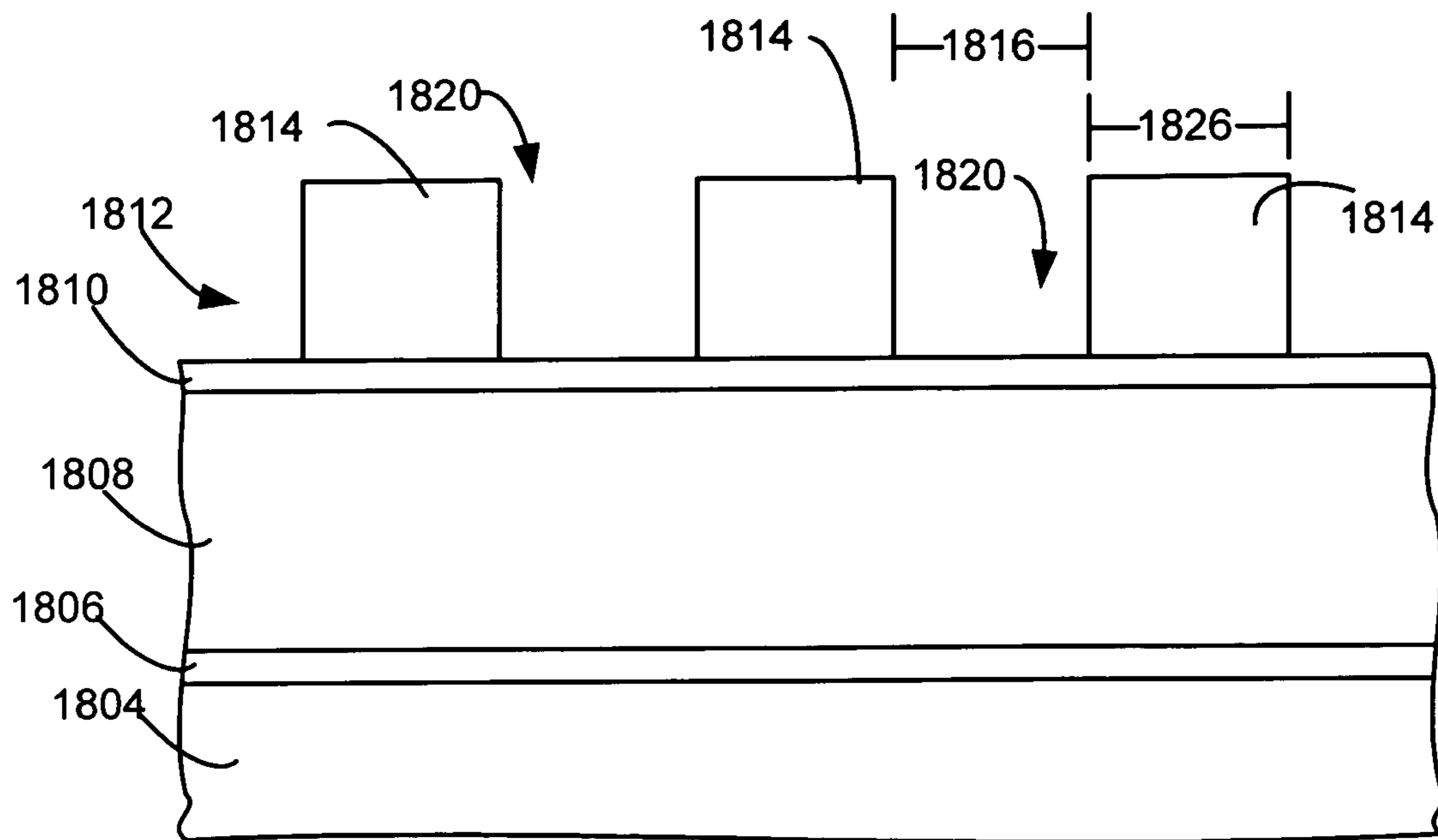


FIG. 12A

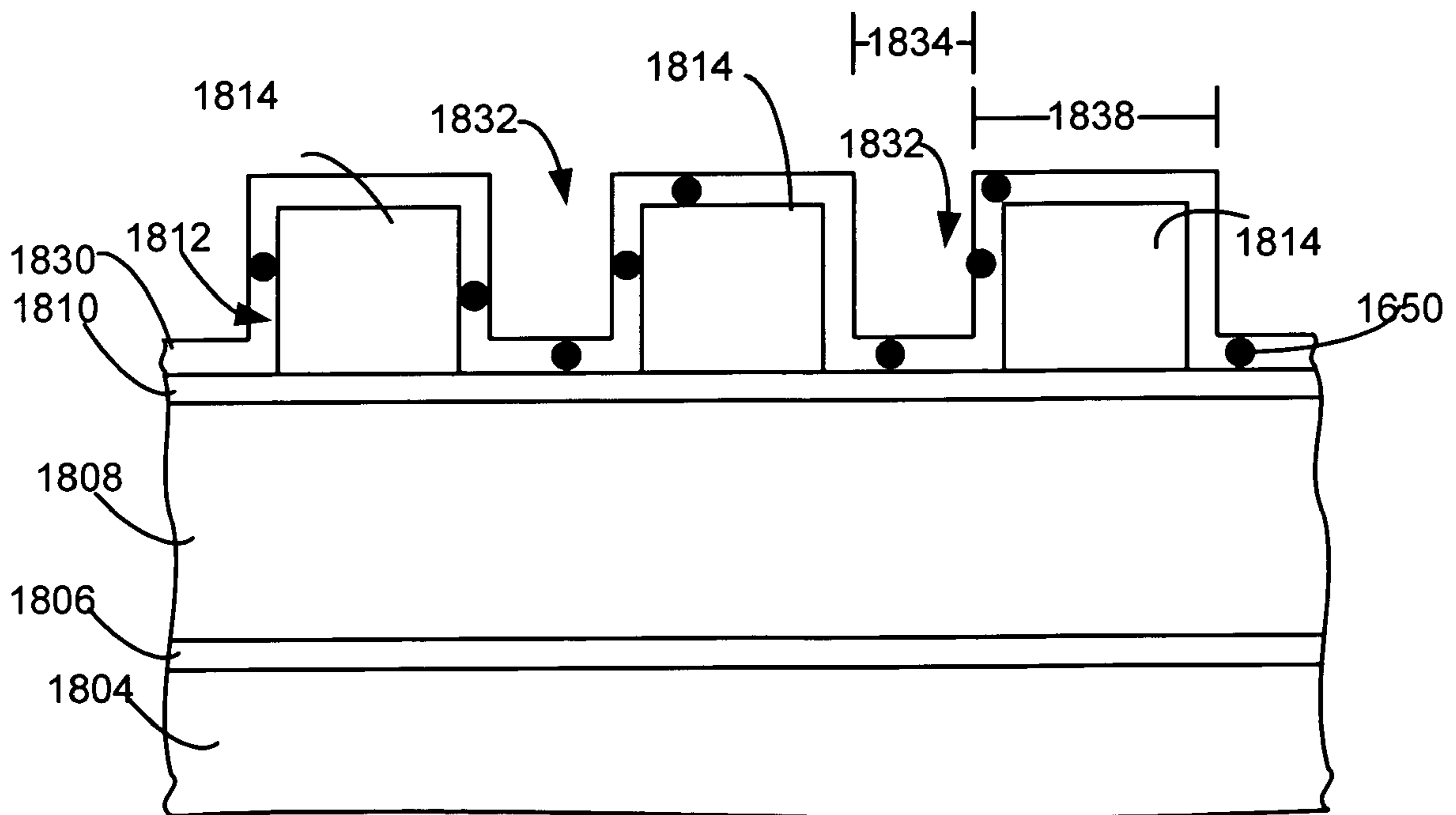


FIG. 12B

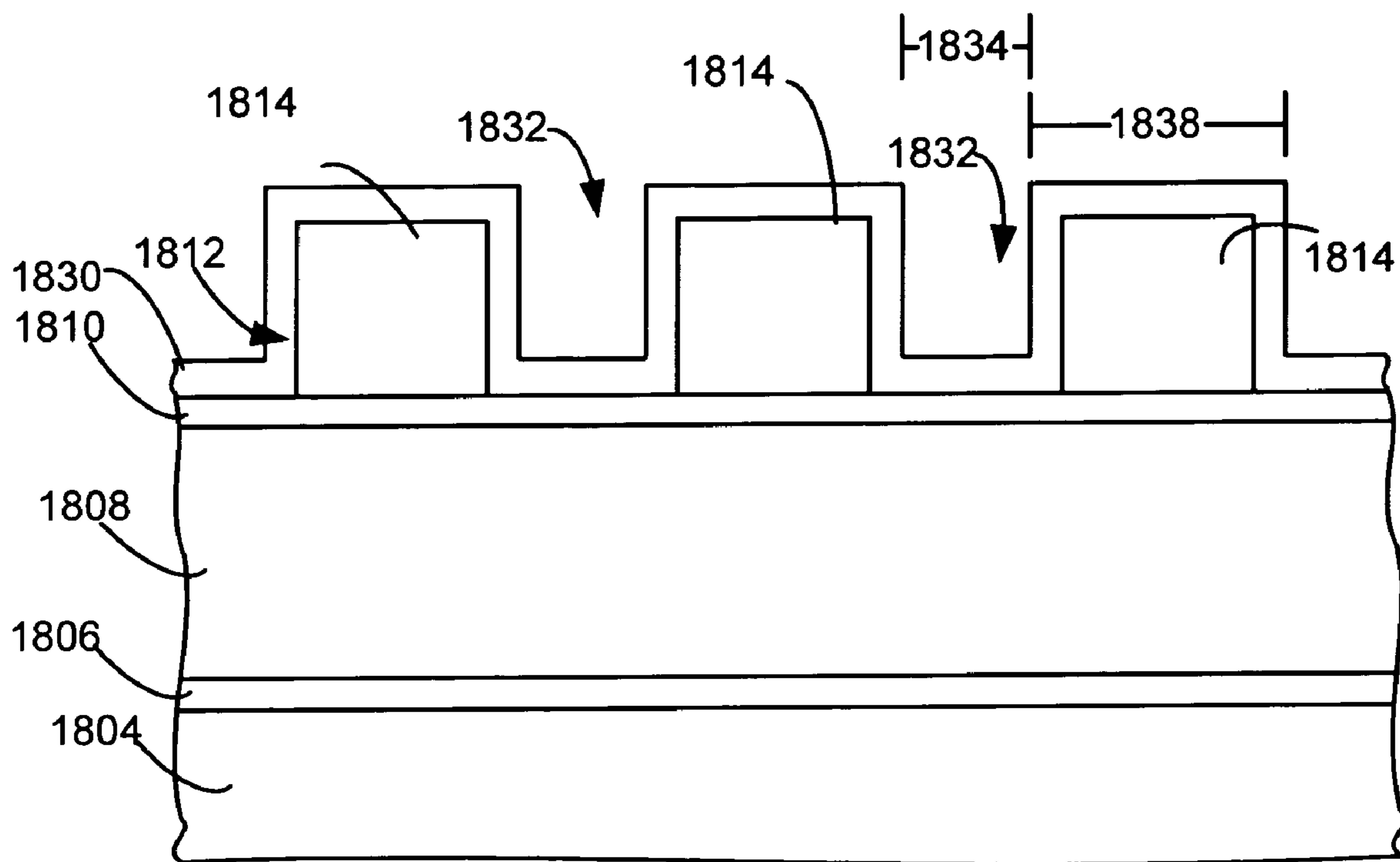


FIG. 12C

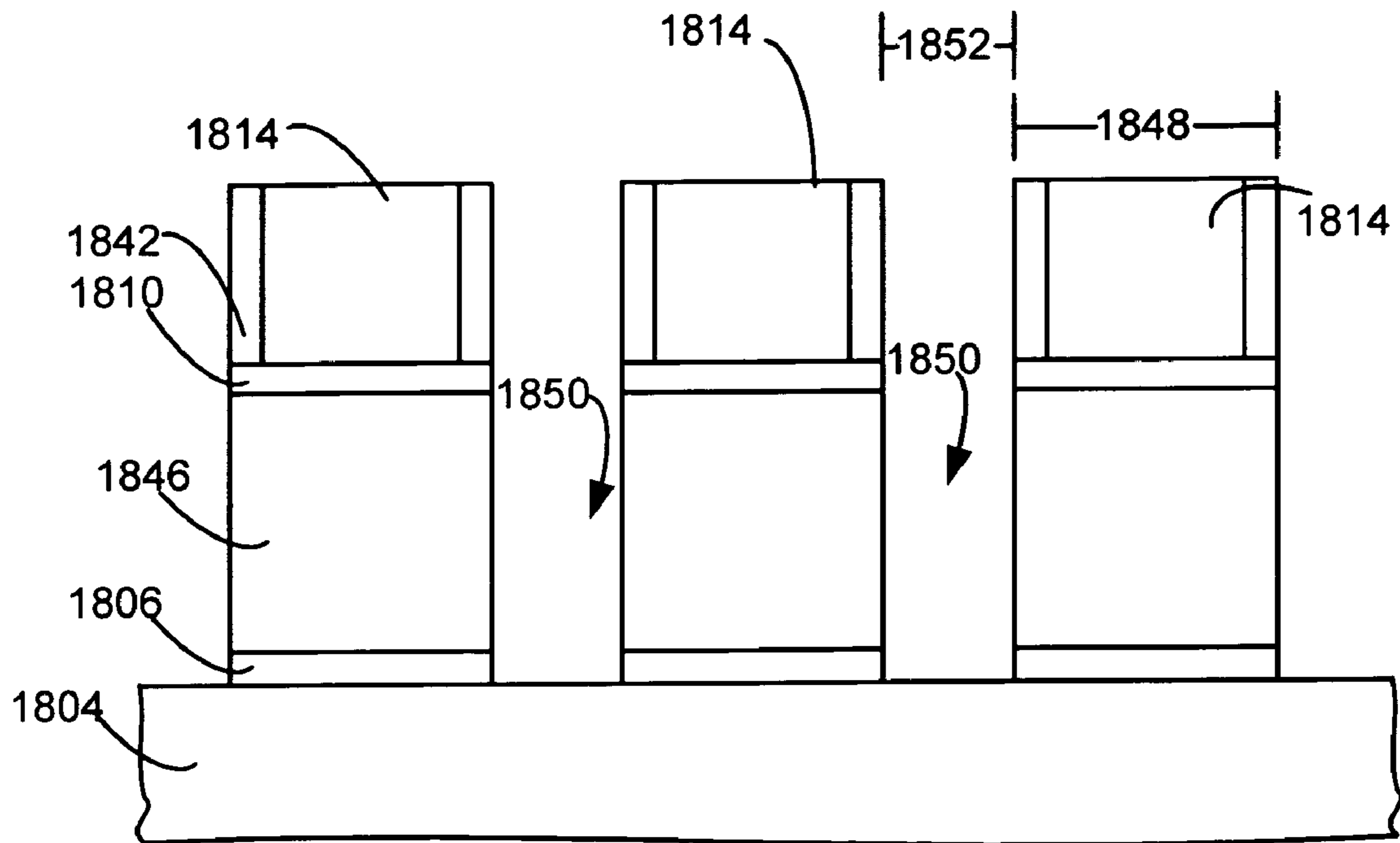


FIG. 12D

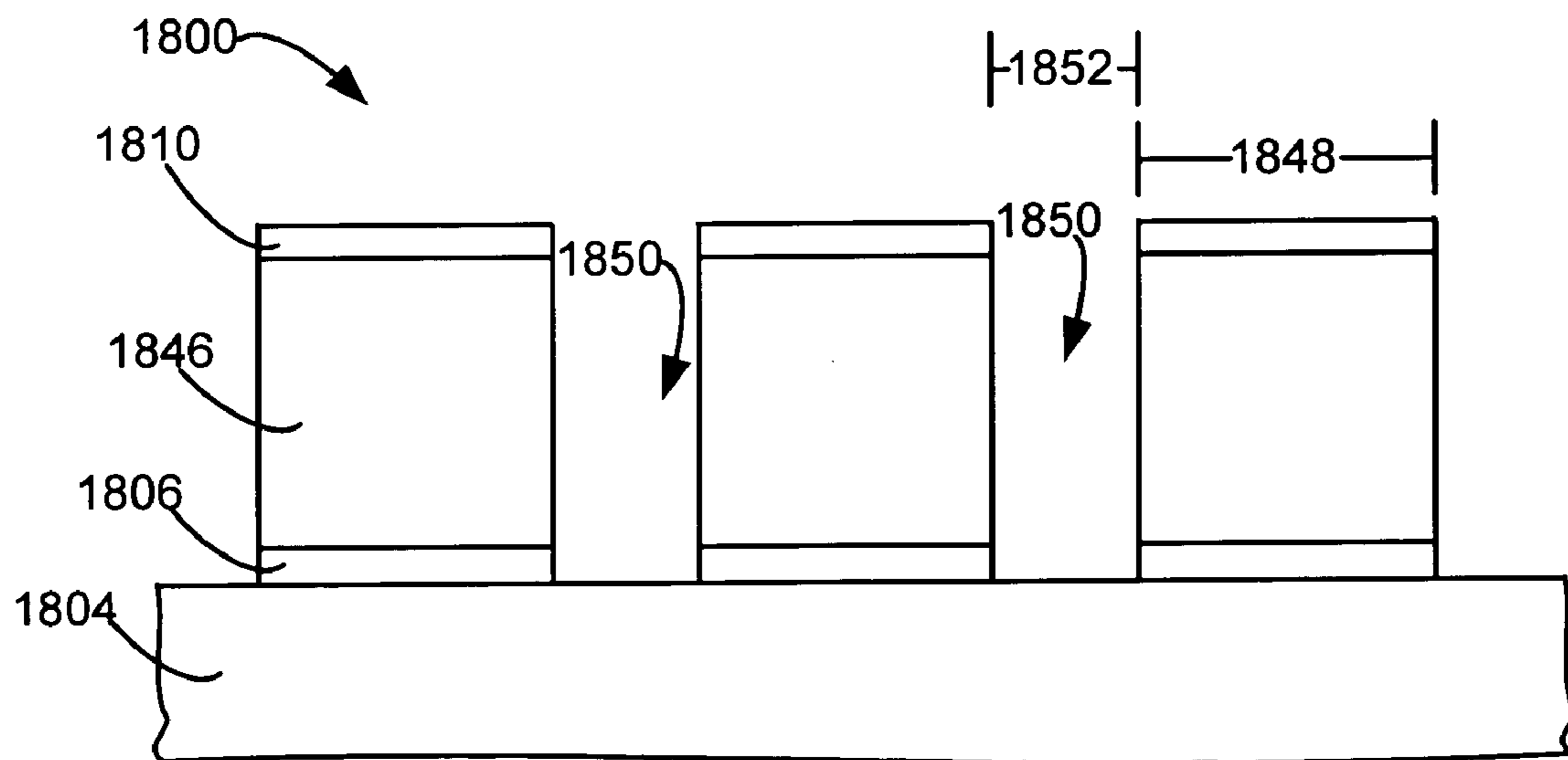


FIG. 12E

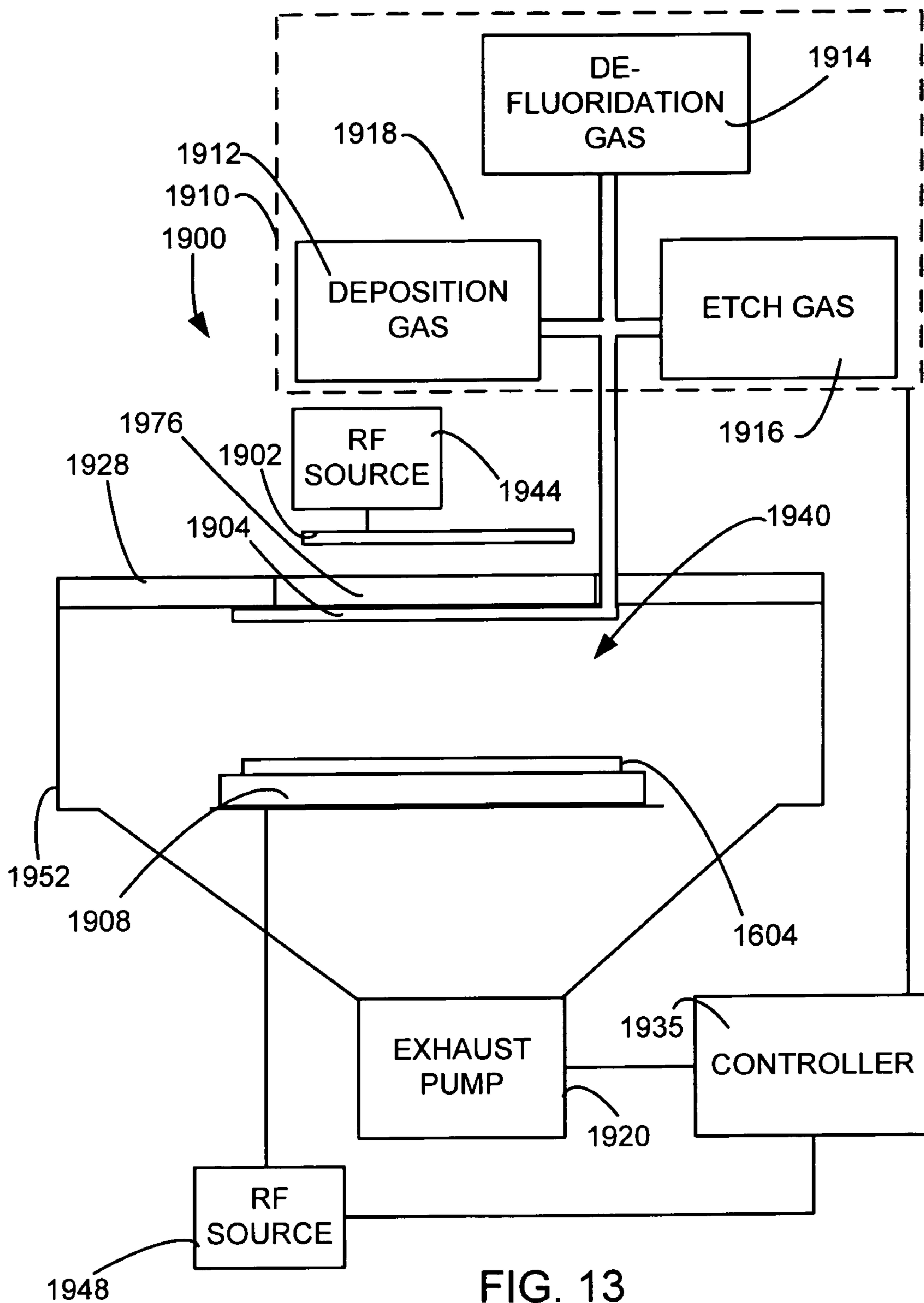


FIG. 13

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DE-FLUORIDATION PROCESS

BACKGROUND OF THE INVENTION

The present invention relates to the formation of semiconductor devices.

During semiconductor wafer processing, features of the semiconductor device are defined in the wafer using well-known patterning and etching processes. In these processes, a photoresist (PR) material is deposited on the wafer and then is exposed to light filtered by a reticle. The reticle is generally a glass plate that is patterned with exemplary feature geometries that block light from propagating through the reticle.

After passing through the reticle, the light contacts the surface of the photoresist material. The light changes the chemical composition of the photoresist material such that a developer can remove a portion of the photoresist material. In the case of positive photoresist materials, the exposed regions are removed, and in the case of negative photoresist materials, the unexposed regions are removed. Thereafter, the wafer is etched to remove the underlying material from the areas that are no longer protected by the photoresist material, and thereby define the desired features in the wafer.

Various generations of photoresist are known. Deep ultra violet (DUV) photoresist is exposed by 248 nm light. To facilitate understanding, FIG. 1A is a schematic cross-sectional view of a layer **108** over a substrate **104**, with a patterned photoresist layer **112**, over an ARL (Anti-reflective layer) **110** over the layer **108** to be etched forming a stack **100**. The photoresist pattern has a critical dimension (CD), which may be the width **116** of the smallest feature. Presently, for 248 nm photoresist a typical CD for the photoresist may be 230-250 nm using conventional processes. Due to optical properties dependent on wavelength, photoresist exposed by longer wavelength light has larger theoretical minimal critical dimensions.

A feature **120** may then be etched through the photoresist pattern, as shown in FIG. 1B. Ideally, the CD of the feature (the width of the feature) is equal to the CD **116** of the feature in the photoresist **112**. In practice, the CD of the feature **116** may be larger than the CD of the photoresist **112** due to faceting, erosion of the photoresist, or undercutting. The feature may also be tapered, where the CD of the feature is at least as great as the CD of the photoresist, but where the feature tapers to have a smaller width near the feature bottom. Such tapering may provide unreliable features.

In order to provide features with smaller CD, features formed using shorter wavelength light are being pursued. 193 nm photoresist is exposed by 193 nm light. Using phase shift reticles and other technology, a 90-100 nm CD photoresist pattern may be formed, using 193 nm photoresist. This would be able to provide a feature with a CD of 90-100 nm. 157 nm photoresist is exposed by 157 nm light. Using phase shift reticles and other technology sub 90 nm CD photoresist patterns may be formed. This would be able to provide a feature with a sub 90 nm CD.

The use of shorter wavelength photoresists may provide additional problems over photoresists using longer wavelengths. To obtain CD's close to the theoretical limit the lithography apparatus should be more precise, which would require more expensive lithography equipment. Presently 193 nm photoresist and 157 nm photoresist may not have selectivities as high as longer wavelength photoresists and may more easily deform under plasma etch conditions.

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In the etching of conductive layers, such as in the formation of memory devices, it is desirable to increase device density without diminishing performance.

SUMMARY OF THE INVENTION

To achieve the foregoing and in accordance with the purpose of the present invention a method for forming a feature in a layer is provided. A photoresist layer is formed over the layer. The photoresist layer is patterned to form photoresist features with photoresist sidewalls, where the photoresist features have a first critical dimension. A fluorine-containing conformal layer is deposited over the sidewalls of the photoresist features to reduce the critical dimensions of the photoresist features. The fluorine contained in the conformal layer is removed, while the remaining material is left in place. Features are etched into the layer, wherein the layer features have a second critical dimension, which is less than the first critical dimension.

In another embodiment of the invention, a method for forming a feature in a layer is provided. A photoresist layer is formed over the layer. The photoresist layer is patterned to form photoresist features with photoresist sidewalls, where the photoresist features have a first critical dimension. A fluorine-containing layer is deposited over the sidewalls of the photoresist features to reduce the critical dimensions of the photoresist features. The depositing layer over the sidewalls of the photoresist feature, comprises, a first deposition with a first gas chemistry to form a first deposition plasma, and a second deposition with a second gas chemistry to form a second deposition plasma, wherein the first gas chemistry is different than the second gas chemistry. The fluorine contained in the deposited layer is removed, while the rest of the deposited layer is left in place. Features are etched into the layer, wherein the layer features have a second critical dimension, wherein the second critical dimension is not greater than 70% of the first critical dimension.

In another embodiment of the invention an apparatus for forming a feature in a layer, wherein the layer is supported by a substrate and wherein the layer is covered by a photoresist mask with photoresist features with a first CD is provided. A plasma processing chamber, comprises a chamber wall forming a plasma processing chamber enclosure, a substrate support for supporting a substrate within the plasma processing chamber enclosure, a pressure regulator for regulating the pressure in the plasma processing chamber enclosure, at least one electrode for providing power to the plasma processing chamber enclosure for sustaining a plasma, a gas inlet for providing gas into the plasma processing chamber enclosure, and a gas outlet for exhausting gas from the plasma processing chamber enclosure. A gas source in fluid connection with the gas inlet comprises a first deposition gas source, a second deposition gas source, a de-fluoridation gas source, and an etchant gas source. A controller controllably connected to the gas source and the at least one electrode comprises at least one processor and computer readable media. The computer readable media comprises computer readable code for providing at least three deposition cycles to form a fluorine-containing sidewall deposition on a photoresist mask to form features with a second CD, within the photoresist features, computer readable code for removing the fluorine contained in the sidewall deposition, computer readable code for providing a flow of an etchant gas from the etchant gas source to the plasma processing chamber after completion of the at least three deposition cycles, and computer readable code for etching features in the layer, using the etchant gas wherein

the features in the layer have a third CD. The computer code for providing at least three deposition cycles to form a sidewall deposition on a photoresist mask to form features with a second CD within the photoresist features comprises computer readable code for providing a flow of a first deposition gas from the first deposition gas source to the plasma processing chamber enclosure, computer readable code for stopping the flow of the first deposition gas from the first deposition gas source to the plasma processing chamber enclosure, computer readable code for providing a flow of a second deposition gas from the second deposition gas source to the plasma processing chamber enclosure after the flow of the first deposition gas is stopped, and computer readable code for stopping the flow of the second deposition gas from the second deposition gas source to the plasma processing chamber enclosure.

In another embodiment of the invention a method of forming a plurality of conductive lines is provided. A conductive layer is placed over a substrate. A mask is formed, where the mask defines a plurality of mask lines with mask spaces between the mask lines, where the mask spaces have a width and wherein the mask lines have a width and have sidewalls. A fluorine-containing conformal layer is deposited over the sidewalls of the mask. The fluorine contained in the conformal layer is removed, while the rest of the conformal layer is left in place. The conductive layer is etched through the mask to form conductive lines and spaces between the conductive lines, where the conductive lines have a width and the spaces between the conductive lines have widths, where the widths of the spaces between the conductive lines is less than the widths of the mask spaces, and where the widths of the conductive lines is greater than the widths of the line masks.

These and other features of the present invention will be described in more detail below in the detailed description of the invention and in conjunction with the following figures.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which like reference numerals refer to similar elements and in which:

FIGS. 1A-B are schematic cross-sectional views of a stack etched according to the prior art.

FIG. 2 is a high level flow chart of a process that may be used in an embodiment of the invention.

FIGS. 3A-E are schematic cross-sectional views of a stack processed according to an embodiment of the invention.

FIG. 4 is a more detailed flow chart of the step of depositing a layer over sidewalls of photoresist features to reduce CD.

FIG. 5 is a schematic view of a plasma processing chamber that may be used in practicing the invention.

FIG. 6 is a schematic cross-sectional view of a deposition layer where only a first deposition phase deposition is used for an entire deposition layer.

FIG. 7 is a schematic cross-sectional view of a deposition layer where only the second deposition phase deposition is used for an entire deposition layer.

FIGS. 8A-B illustrate a computer system, which is suitable for implementing a controller used in embodiments of the present invention.

FIGS. 9A-C are cross-sectional views of photoresist masks for producing conductive lines, according to the prior art.

FIGS. 10A-F are schematic cross-sectional views of a conductive layer processed according to an embodiment of the invention.

FIG. 11 is a flow chart of an etch step.

FIGS. 12A-E are schematic cross-sectional views of a conductive layer processed according to an embodiment of the invention.

FIG. 13 is a schematic illustration of a device that may be used for practicing the invention for etching conductive layers.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will now be described in detail with reference to a few preferred embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present invention.

The invention provides features with small critical dimensions (CD). More specifically, the invention provides features with CD's that are less than the CD of the photoresist pattern used to etch the feature.

To facilitate understanding, FIG. 2 is a high level flow chart of a process that may be used in an embodiment of the invention. A patterned photoresist mask is provided (step 204). FIG. 3A is a schematic cross-sectional view of a layer to be etched 308 over a substrate 304, with a patterned photoresist mask 312 with a feature 314, over an ARL 310, over the layer 308 to be etched forming a stack 300. The photoresist mask has a photoresist feature critical dimension (CD), which may be the widest part of the width 316 of the smallest possible feature. Presently, for 248 nm photoresist a typical CD for the photoresist may be 230-250 nm, using conventional processes.

A layer is then deposited over the sidewalls of the photoresist features to reduce the CD (step 208). FIG. 3B is a schematic cross-sectional view of the patterned photoresist mask 312 with a fluorine-containing layer 320 deposited over the sidewalls of the feature 314. Various types of materials may be used to form the fluorine-containing deposited layer 320 over the sidewalls of the photoresist mask 312. One preferred choice is to use fluorine-based chemistries, which deposit fluorine-included polymer, such as fluorocarbon polymer (with CH₃F gas). The fluorine-containing deposited layer 320 contains fluorine molecules 350, as well as other types of materials.

The fluorine-containing deposited layer 320 forms a deposited layer feature 322 within the photoresist feature 314, where the deposited layer feature 322 has a reduced CD 324 that is less than the CD 316 of the photoresist feature 314. Preferably, the reduced CD 324 of the deposited layer feature 322 is at least 30% less than the CD 316 of the photoresist feature (i.e. not greater than 70% of the CD 316 of the photoresist feature). More preferably, the reduced CD 324 of the deposited layer feature 322 is at least 40% less than the CD 316 of the photoresist feature (i.e. not greater than 60% of the CD 316 of the photoresist feature). Most preferably, the reduced CD 324 of the deposited layer feature 322 is at least 50% less than the CD 316 of the photoresist feature (i.e. not greater than 50% of the CD 316

of the photoresist feature). For example, the deposited layer feature may have a reduced CD **316** that is 99% less than the CD **316** of the photoresist feature. It is also desirable that the deposited layer feature **322** has substantially vertical sidewalls **328**, which are highly conformal as shown. An example of a substantially vertical sidewall is a sidewall that from bottom to top makes an angle of between 88° to 90° with the bottom of the feature. Conformal sidewalls have a deposition layer that has substantially the same thickness from the top to the bottom of the feature. Non-conformal sidewalls may form a faceting or a bread-loafing formation, which provide non-substantially vertical sidewalls. Tapered sidewalls (from the faceting formation) or bread-loafing sidewalls may increase the deposited layer CD and provide a poor etching mask. Preferably, the deposition on the side wall is thicker than the deposition on the bottom of the photoresist feature. More preferably, no layer is deposited over the bottom of the photoresist feature.

When the fluorine-containing layer **320** is formed using fluorine-included polymer, during the subsequent etching process, chemical reactions between the fluorine-included polymer and the gas used for etching increases the removal of the polymer due to the presence of the fluorine **350** in the fluorine-included polymer. Thus, it is desirable to remove the fluorine **350** from the deposited conformal layer **320** before the etching step in order to prevent the fluorine **350** included in the fluorine-containing deposited layer **320** from interfering with the subsequent etching process.

Fluorine included in the deposited layer is removed **320** (step **210**). FIG. 3C is a schematic cross-sectional view of removing the fluorine from the deposited layer **320**. In one embodiment of the invention, when the fluorine-containing deposited layer **320** is formed using fluorine-included polymer, the fluorine **350** is first removed from the deposited layer **320** by applying the nitrogen/oxygen plasma treatment to the deposited layer **320**. This is called the de-fluoridation (DF) process.

In one embodiment of the invention, a combination of nitrogen/oxygen gas is charged and becomes nitrogen/oxygen plasma. The nitrogen/oxygen plasma is contained in a plasma chamber. The fluorine-included polymer, which forms the deposited layer **320**, is then treated with the nitrogen/oxygen plasma. This results in a plasma-driven chemical reaction between the nitrogen/oxygen plasma and the fluorine-included polymer. One effect of the chemical reaction is that the fluorine molecules **350** in the fluorine-included polymer are released, and thus removed from the polymer that forms the deposited layer **320**, while leaving the remaining polymer still in place.

With respect to the nitrogen/oxygen gas combination, in one embodiment of the invention, preferably, the ratio between nitrogen and oxygen should be within the range from 10-part nitrogen to 1-part oxygen (10:1) to 1-part nitrogen to 10-part oxygen (1:10) by volume. More preferably, the ratio between nitrogen and oxygen should be within the range from 3-part nitrogen to 1-part oxygen (3:1) to 1-part nitrogen to 1-part oxygen (1:1). Most preferably, the ratio between nitrogen and oxygen should be 2-part nitrogen to 1-part oxygen (2:1). In another embodiment of the invention, there should be more nitrogen gas than oxygen gas.

In one embodiment of the invention, the nitrogen gas flows into the plasma chamber at a rate of 50 standard-cubic-centimeters-per-minute (sccm) and the oxygen gas flows into the plasma chamber at a rate of 150 sccm.

With respect to the plasma chamber where the de-fluoridation process occurs, preferably, the chamber pressure should be less than 100 milli-Torr (mT). More preferably,

the chamber pressure should be 30 mT. Preferably, the RF power should be between 50 watts to 1000 watts. More preferably, the RF power should be 500 watts of 27 megahertz (MHz) plasma frequency. Preferably, the temperature should be between -50 degrees Celsius (° C.) and 140° C. Preferably, the plasma treatment should last for 10 seconds.

After the fluorine is removed from the fluorine-included deposited layer **320**, features are then etched into the layer to be etched **308** through the deposited layer features **322** (step **212**). FIG. 3D shows a feature **332** etched into the layer to be etched **308**. In this example, the feature **332** etched in the layer to be etched **308** has a CD **336**, which is equal to the CD **324** of the deposited layer feature **322**. In practice, the CD **336** of the feature **332** may be slightly larger than the CD **324** of the feature **322** of the deposited layer **320**. However, since the CD **324** of the deposited layer feature **322** is significantly smaller than the CD **316** of the photoresist **312**, the CD **336** of the feature **332** in the layer to be etched **308** is still smaller than the CD **316** of the photoresist **312**. If the CD **324** of the deposited layer was only slightly smaller than the CD of the photoresist, or if the deposited layer was faceted or bread loafed, then the CD of the layer to be etched might not be smaller than the CD of the photoresist. In addition, a faceted or bread-loafing deposited layer may cause a faceted or irregularly shaped feature in the layer to be etched. It is also desirable to minimize deposition on the bottom of the photoresist feature. Preferably, the CD **336** of the feature **332** etched in the layer to be etched **308** is at least 30% less than the CD **316** of the photoresist feature. More preferably, the CD **336** of the feature **332** etched in the layer to be etched **308** is at least 40% less than the CD **316** of the photoresist feature. Most preferably, the CD **336** of the feature **332** etched in the layer to be etched **308** is at least 50% less than the CD **316** of the photoresist feature.

The photoresist and deposited layer may then be stripped (step **216**). This may be done as a single step or two separate steps with a separate deposited layer removal step and photoresist strip step. Ashing may be used for the stripping process. FIG. 3E shows the stack **300** after the deposited layer and photoresist mask have been removed. Additional formation steps may be performed (step **220**). For example, a contact **340** may then be formed in the feature. To provide a dual damascene structure, a trench may be etched before the contact is formed. Additional processes may be performed after the contact is formed.

FIG. 4 is a more detailed flow chart of the deposit layer over sidewalls of photoresist features to reduce CD step **208**. In the embodiment, the deposit layer over sidewalls of photoresist features to reduce CD step **208** comprises a first deposition phase **404** and a second deposition phase **408**.

Example of Dielectric Etch

FIG. 5 is a schematic view of a plasma processing chamber **500** that may be used for depositing the layer, de-fluoridation, etching, and stripping. The plasma processing chamber **500** comprises confinement rings **502**, an upper electrode **504**, a lower electrode **508**, a gas source **510**, and an exhaust pump **520**. The gas source **510** comprises a first deposition gas source **512** and a second deposition gas source **516**. In one embodiment of the invention, the gas source **510** may comprise additional gas sources, such as a de-fluoridation gas source **514** and an etching gas source **518**. In another embodiment of the invention, separate plasma processing chambers are used for depositing the layer, de-fluoridation, etching, and stripping.

Within plasma processing chamber **500**, the substrate **304** is positioned upon the lower electrode **508**. The lower

electrode **508** incorporates a suitable substrate chucking mechanism (e.g., electrostatic, mechanical clamping, or the like) for holding the substrate **304**. The reactor top **528** incorporates the upper electrode **504** disposed immediately opposite the lower electrode **508**. The upper electrode **504**, lower electrode **508**, and confinement rings **502** define the confined plasma volume. Gas is supplied to the confined plasma volume by the gas source **510** and is exhausted from the confined plasma volume through the confinement rings **502** and an exhaust port by the exhaust pump **520**. A first RF source **544** is electrically connected to the upper electrode **504**. A second RF source **548** is electrically connected to the lower electrode **508**. Chamber walls **552** surround the confinement rings **502**, the upper electrode **504**, and the lower electrode **508**. Both the first RF source **544** and the second RF source **548** may comprise a 27 MHz power source and a 2 MHz power source. Different combinations of connecting RF power to the electrode are possible. In the case of Exelan HPT™, which is basically the same as an Exelan HP with a Turbo Pump attached to the chamber, made by LAM Research Corporation™ of Fremont, Calif., which may be used in a preferred embodiment of the invention, both the 27 MHz and 2 MHz power sources make up the second RF power source **548** connected to the lower electrode, and the upper electrode is grounded. A controller **535** is controllably connected to the RF sources **544**, **548**, exhaust pump **520**, and the gas source **510**. The Exelan HPT would be used when the layer to be etched **308** is a dielectric layer, such as silicon oxide or organo silicate glass.

FIGS. **8A** and **8B** illustrate a computer system **1300**, which is suitable for implementing a controller **535** used in embodiments of the present invention. FIG. **8A** shows one possible physical form of the computer system. Of course, the computer system may have many physical forms ranging from an integrated circuit, a printed circuit board, and a small handheld device up to a huge super computer. Computer system **1300** includes a monitor **1302**, a display **1304**, a housing **1306**, a disk drive **1308**, a keyboard **1310**, and a mouse **1312**. Disk **1314** is a computer-readable medium used to transfer data to and from computer system **1300**.

FIG. **8B** is an example of a block diagram for computer system **1300**. Attached to system bus **1320** is a wide variety of subsystems. Processor(s) **1322** (also referred to as central processing units, or CPUs) are coupled to storage devices, including memory **1324**. Memory **1324** includes random access memory (RAM) and read-only memory (ROM). As is well known in the art, ROM acts to transfer data and instructions uni-directionally to the CPU and RAM is used typically to transfer data and instructions in a bi-directional manner. Both of these types of memories may include any suitable of the computer-readable media described below. A fixed disk **1326** is also coupled bi-directionally to CPU **1322**; it provides additional data storage capacity and may also include any of the computer-readable media described below. Fixed disk **1326** may be used to store programs, data, and the like and is typically a secondary storage medium (such as a hard disk) that is slower than primary storage. It will be appreciated that the information retained within fixed disk **1326** may, in appropriate cases, be incorporated in standard fashion as virtual memory in memory **1324**. Removable disk **1314** may take the form of any of the computer-readable media described below.

CPU **1322** is also coupled to a variety of input/output devices, such as display **1304**, keyboard **1310**, mouse **1312** and speakers **1330**. In general, an input/output device may be any of: video displays, track balls, mice, keyboards, microphones, touch-sensitive displays, transducer card read-

ers, magnetic or paper tape readers, tablets, styluses, voice or handwriting recognizers, biometrics readers, or other computers. CPU **1322** optionally may be coupled to another computer or telecommunications network using network interface **1340**. With such a network interface, it is contemplated that the CPU might receive information from the network, or might output information to the network in the course of performing the above-described method steps. Furthermore, method embodiments of the present invention may execute solely upon CPU **1322** or may execute over a network such as the Internet in conjunction with a remote CPU that shares a portion of the processing.

In addition, embodiments of the present invention further relate to computer storage products with a computer-readable medium that have computer code thereon for performing various computer-implemented operations. The media and computer code may be those specially designed and constructed for the purposes of the present invention, or they may be of the kind well known and available to those having skill in the computer software arts. Examples of computer-readable media include, but are not limited to: magnetic media such as hard disks, floppy disks, and magnetic tape; optical media such as CD-ROMs and holographic devices; magneto-optical media such as floptical disks; and hardware devices that are specially configured to store and execute program code, such as application-specific integrated circuits (ASICs), programmable logic devices (PLDs) and ROM and RAM devices. Examples of computer code include machine code, such as produced by a compiler, and files containing higher level code that are executed by a computer using an interpreter. Computer readable media may also be computer code transmitted by a computer data signal embodied in a carrier wave and representing a sequence of instructions that are executable by a processor.

Other examples may use other deposition devices.

One example of a first deposition phase **404** may be CH_3F deposition using a chemistry of 250 sccm (standard cubic centimeters per minute) Ar and 50 sccm CH_3F , at a pressure of 60 mTorr, established by setting a Vat valve of the turbo pump to 1000. The 27 MHz RF source provides 500 Watts of power, while the 2 MHz RF source provides 100 Watts of power. The chamber temperature is maintained at 20° C. A helium cooling pressure, to cool the substrate is 15 Torr.

One example of a second deposition phase **408** may be $\text{C}_4\text{F}_6/\text{O}_2/\text{CO}$ deposition using a chemistry of 270 sccm Ar, 12 sccm C_4F_6 , 8 sccm O_2 , and 100 sccm CO, at a pressure of 50 mTorr, established by setting a Vat valve of the turbo pump to 1000. The 27 MHz RF source provides 1500 Watts of power, while the 2 MHz RF source provides 480 Watts of power. The chamber temperature is maintained at 20° C. A helium cooling pressure, to cool the substrate is 15 Torr.

FIG. **6** is a schematic cross-sectional view of a deposition layer **620** where only the first deposition phase deposition is used for an entire deposition layer **620**. The deposition layer **620** is formed over a photoresist mask **612**, over an ARL **610**, over a layer to be etched **608**, over a substrate **604**. The photoresist mask **612** forms a feature **614**. In this example, the first deposition forms a "bread-loafing" deposition layer. The bread-loafing deposition layer is characterized by a thicker sidewall deposition **636** near the top of the feature and a thinner (or no) sidewall deposition **632** near the bottom of the feature. Therefore, this deposition provides a non-conformal sidewall deposition. Such a deposition does not provide the desired substantially vertical sidewalls. The bread-loafing eventually pinches off the top, which then cannot be used as a masking layer, since the contact will be closed off and no etching can be done.

FIG. 7 is a schematic cross-sectional view of a deposition layer 720 where only the second deposition phase deposition is used for an entire deposition layer 720. The deposition layer 720 is formed over a photoresist mask 712, over an ARL 710, over a layer to be etched 708, over a substrate 704. The photoresist mask 712 forms a feature 714. In this example, the first deposition forms a “faceting” deposition layer. The faceting deposition layer is characterized by a thinner (or no) sidewall deposition 732 near the top of the feature and a thicker sidewall deposition 736 near the bottom of the feature. Therefore, this deposition also provides a non-conformal sidewall deposition. If the sidewalls near the top are too thin, faceting 740 of the photoresist mask 712 may result. Such a deposition does not provide the desired substantially vertical sidewalls. The faceting of the corners of the photoresist mask may cause lower etch selectivity and fast mask erosion. The faceting of the mask will also result in faceting of the etched profile. In almost all cases, once the mask is faceted, then the final etched profile is also faceted, since the mask vertical profile generally translates into the etched material.

Therefore in an example of a preferred embodiment of the invention, the first deposition phase 404 and the second deposition phase 408 in the example above are alternated for 6 cycles, where the first deposition phase 404 is for 2 seconds and the second deposition phase 408 is for 25 seconds. Such a deposition would have a first deposition of the first deposition phase 404, and then a second deposition of the second deposition phase 408, then a third deposition of the first deposition phase 404, then a fourth deposition of the second deposition phase 408, which is repeated until there is a twelfth deposition.

The ability to control the ratio of etch times of the first deposition phase 404 and the second deposition phase 408 provide another control variable. A proper ratio will provide substantially vertical and conformal sidewalls as illustrated in FIG. 3B. Such a deposition layer is also able to protect the photoresist mask to increase etch selectivity. Other control parameters provided by the invention that can be used to control the deposition profiles are: number of cycles, total deposition time, deposition1/deposition2 time ratio, gas chemistry ratio (such as $\text{CH}_3\text{F}/\text{O}_2$ ratio or $\text{C}_4\text{F}_6/\text{O}_2$ ratio). Other gas chemistries such as CH_2F_2 instead of CH_3F or C_4F_8 instead of C_4F_6 , etc. may be used.

The ability to form features with smaller critical dimensions, without changing the photoresist, allows for smaller features without purchasing new lithography equipment. In newer generations of photoresist are used, the invention provides small CD's for the newer generations of photoresist.

In other embodiments, three or more different gas chemistries may be used providing three or more different deposition phases.

Example of Conductive Layer Etch

In the formation of conductive lines, such as metal connectors or memory devices like flash memory, it is desirable to increase the thickness of the conductive lines and/or decrease the CD of the spacing between the conductive lines. FIG. 9 A is a cross-sectional view of a photoresist mask for producing conductive lines, when spacing between the lines is too close according to the prior art. Over a substrate 1504, such as a wafer a barrier layer 1506 may be placed. Over the barrier layer 1506 a conductive layer 1508 such as a metal layer or a polysilicon layer is formed. Over the conductive layer 1508 an antireflective layer (ARL) 1510 such as a DARC layer is formed. A photoresist mask 1512 is formed over the ARL 1510. In this example, the

photoresist mask 1512 forms line masks 1514 with photoresist residue 1518 formed in spaces between the line masks 1514. The presence of the photoresist residue 1518 is caused by providing too small of a space between the line masks 1514, since it is more difficult to remove residue from a small space. This may limit the density of the conductive lines that may be provided.

FIG. 9B is another cross-sectional view of a photoresist mask 1512b for producing conductive lines, used in the prior art to attempt to overcome the problem created by too small spacing. The line masks 1514b in this example are made thinner to allow wider spaces 1520 to prevent resist residue and maintain the same pitch or density as the previous example. One of the drawbacks of this approach is that thinner line masks 1514b result in thinner lines. The thinner lines may result in less reliability and poorer performance. The thinner lines may result in smaller transistor areas, which may cause a short channel effect and other performance problems, such as short channel effect and high wordline resistance (causing a slower speed)).

FIG. 9C is another cross-sectional view of a photoresist mask 1512c for producing conductive lines, used in the prior art to attempt to overcome the problem created by too small spacing. In some applications, it is desirable that the line masks 1514c have the same width as the spaces 1522. Since in this example, the spaces 1522 are made wider to prevent resist residue, the line masks 1514c are also wider. As a result, the pitch is increased and the density of the lines is decreased.

It is desirable to provide more densely placed conductive lines by reducing spacing between lines while maintaining wider line widths.

The high level process shown in FIG. 2 will be used to facilitate the understanding of this embodiment of the invention. A patterned photoresist mask is provided (step 204). FIG. 10A is a schematic cross-sectional view of a conductive layer to be etched 1608 over a barrier layer 1606 over a substrate 1604, with a patterned photoresist mask 1612 forming mask lines 1614, with mask spaces 1620 therebetween, over an ARL 1610, over the conductive layer 1608 to be etched. The photoresist mask has a space critical dimension (CD), which is the width 1616 of the space, and a line CD, which is the width 1626 of the mask lines 1614. Presently, for 248 nm photoresist a typical CD for the space width CD is 0.16 μm . Generally, the width of the space in the photoresist is made wide enough to provide the formation of the space in the photoresist without photoresist residue in the space. The width of the photoresist mask lines is thin enough to provide an increase density of conductive lines.

A fluorine-containing conformal layer is then deposited over the sidewalls of the photoresist features to reduced the width of the space (step 208). FIG. 10B is a schematic cross-sectional view of the patterned photoresist mask 1612 with a layer 1630 deposited over the sidewalls of the mask 1612. The deposited layer 1630 contains fluorine 1650. The fluorine-containing deposited layer 1630 forms a deposited layer space 1632 within the mask space, where the deposited layer space 1632 has a reduced width (CD) 1634 that is less than the width 1616 of the mask space. In addition, the fluorine-containing deposited layer 1630 forms deposited layer mask lines with a width 1638 that is greater than the width 1626 of the mask lines 1614. Preferably, the reduced width 1634 of the deposited layer space 1632 is at least 20% less than the width 1616 of the mask space 1620 (i.e. not greater than 80% of the width 1616 of the mask space 1620). More preferably, the reduced width 1634 of the deposited layer space 1632 is at least 50% less than the width 1616 of

the mask space **1620** (i.e. not greater than 50% of the width **1616** of the mask space **1620**). Most preferably, the reduced width **1616** of the deposited layer space **1632** is at least 70% less than the width **1634** of the mask space **1620** (i.e. not greater than 30% of the width **1616** of the mask space **1620**). It is also desirable that the deposited layer forms substantially vertical sidewalls **1642**, which are highly conformal as shown. An example of a substantially vertical sidewall is a sidewall that from bottom to top makes an angle of between 88° to 90° with the bottom of the space. Conformal sidewalls have a deposition layer that has substantially the same thickness from the top to the bottom of the space. This process for a conductive layer etch is able to provide a conformal layer in a single deposition.

In the preferred embodiment for etching a conductive layer, the fluorine-containing deposition layer is conformal in all directions (isotropic). This results in the layer over the ARL **1610** to be about as thick as the layer on the sidewalls of the mask

The fluorine in the deposited layer **1630** is removed. FIG. **10C** is a schematic cross-sectional view of the patterned photoresist mask **1612** with a layer **1630** deposited over the sidewalls of the mask **1612**, after the fluorine **1650** in the deposited layer **1630** has been removed while leaving the rest of the deposited layer **1630** in place. In one embodiment of the invention, the fluorine-included deposited layer **1630** is treated with a combination of nitrogen/oxygen gas plasma, which results in a plasma-driven chemical reaction between the nitrogen/oxygen plasma and the fluorine-containing deposited layer **1630**. The fluorine molecules **1650** in the deposited layer **1630** are released and thus removed from the deposited layer **1630**, while leaving the rest of the deposited layer **1630** still in place.

The conductive layer **1608** may be etched through the deposited layer **1630** (step **212**). In this example, the etching step comprises at least two separate etches, as illustrated in FIG. **11**. An anisotropic deposition layer etch is used to etch the deposited layer **1630** (step **1704**). FIG. **16D** is a cross-sectional view of the substrate after the deposited layer is anisotropically etched. The remaining deposited layer forms sidewalls **1642** around the mask lines **1614**. An anisotropic conductive layer etch is used to etch into the conductive layer **1608** (step **1708**).

FIG. **10E** is a cross-sectional view of the substrate after the conductive layer is etched to form conductive lines **1646** with spaces **1650** formed therebetween. The conductive lines **1646** have a width **1648** and the spaces between the conductive lines have a width **1652**, as shown in FIG. **10E**. Preferably, the width **1652** of the space **1650** between the conductive lines is at least 20% less than the width **1616** of the space **1620** between the mask lines. More preferably, the width **1652** of the space **1650** between the conductive lines is at least 50% less than the width **1616** of the space **1620** between the mask lines. Most preferably, the width **1652** of the space **1650** between the conductive lines is at least 70% less than the width **1616** of the space **1620** between the mask lines.

The photoresist and deposited layer may then be stripped (step **216**). This may be done as a single step or two separate steps with a separate deposited layer removal step and photoresist strip step. Ashing may be used for the stripping process. FIG. **10F** shows the stack **1600** after the deposited layer and photoresist mask have been removed. Additional processes may be performed (step **220**). For example, the conductive lines may be formed to be part of a memory device.

The resulting structure provides a higher density device with smaller spacing and wider conductive lines. In this example, the widths **1648** of the conductive lines **1646** are about equal to the widths **1652** of the spaces **1650**. Other conductive line width to space width ratios may be provided by this embodiment. Preferably, the ratio of the width of the mask line to the width of the space between mask lines is less than 1:1, where the ratios of the width of the conductive line to the space between the conductive line is not less than 1:1, and even more preferably greater than 1:1. Such ratios may be useful in providing higher density memory devices, where the conductive layer is a polysilicon.

In another embodiment of the invention, the mask lines have a width that is about equal to the width of the space. FIG. **12A** is a cross-sectional view of a conductive layer to be etched **1808** over a barrier layer **1806** over a substrate **1804**, with a patterned photoresist mask **1812** forming mask lines **1814**, with mask spaces **1820** therebetween, over an ARL **1810**, over the conductive layer **1808** to be etched. The photoresist mask has a space critical dimension (CD), which is the width **1816** of the space, and a line CD, which is the width **1826** of the mask lines **1814**. Generally, the width of the space in the photoresist is made wide enough to provide the formation of the space in the photoresist without photoresist residue in the space.

A fluorine-containing conformal layer is then deposited over the sidewalls of the photoresist features to reduce the width of the space (step **208**). FIG. **1812B** is a schematic cross-sectional view of the patterned photoresist mask **1812** with a layer **1830** deposited over the sidewalls of the mask **1812**. The deposited layer **1830** contains fluorine **1850**. The fluorine-containing deposited layer **1830** forms a deposited layer space **1832** within the mask space, where the deposited layer space **1832** has a reduced width (CD) **1834** that is less than the width **1816** of the mask space. In addition, the fluorine-containing deposited layer **1830** forms deposited layer mask lines with a width **1838** that is greater than the width **1826** of the mask lines **1814**.

The fluorine in the deposited layer **1830** is removed. FIG. **12C** is a schematic cross-sectional view of the patterned photoresist mask **1812** with a layer **1330** deposited over the sidewalls of the mask **1812**, after the fluorine **1850** in the deposited layer **1830** has been removed while leaving the rest of the deposited layer **1830** in place. In one embodiment of the invention, the fluorine-included deposited layer **1830** is treated with a combination of nitrogen/oxygen gas plasma, which results in a plasma-driven chemical reaction between the nitrogen/oxygen plasma and the fluorine-containing deposited layer **1830**. The fluorine molecules **1850** in the deposited layer **1830** are released and thus removed from the deposited layer **1830**, while leaving the rest of the deposited layer **1830** still in place.

The conductive layer **1808** may be etched through the deposited layer **1830** (step **212**). FIG. **18D** is a cross-sectional view of the substrate after the conductive layer is etched to form conductive lines **1846** with spaces **1850** formed therebetween. The conductive lines **1846** have a width **1848** and the spaces between the conductive lines have a width **1852**, as shown in FIG. **12D**.

The photoresist and deposited layer may then be stripped (step **216**). FIG. **12E** shows the stack **1800** after the deposited layer and photoresist mask have been removed. Additional processes may be performed (step **220**). For example, the metal lines may be used for electrically connecting various devices.

The resulting structure provides wider conductive wires that are more closely spaced. In this example, although the

conductive metal lines may have the same density as done previously, providing wider conductive lines with smaller spacing improves the performance of the conductive lines, such as by providing a reduced resistance. The inventions may provide a conductive line width that is more than 100% greater than the line width of the original mask. More preferably, the conductive line width is more than 150% greater than the line width of the original mask. In this embodiment, the deposition steps are in order and are not simultaneous.

Example Recipe

In an example recipe, a device that may be used for both depositing and etching the deposition layer and the conductive layer is the 2300 Versys™ made by LAM Research Corporation™ of Fremont, Calif. FIG. 13 is a schematic illustration of such a device 1900 used for both depositing and etching the deposition layer. The plasma processing chamber 1900 comprises an inductive antenna (or coil) 1902, a gas distribution plate (GDP) 1904, a substrate support 1908, a gas source 1910, and an exhaust pump 1920. The gas source 1910 is in fluid connection with the gas distribution plate 1904 and comprises a deposition gas source 1912, a de-fluoridation gas 1914, and an etch gas source 1916. The gas source 1910 may comprise additional gas sources, such as a second etching or deposition gas source. Within plasma processing chamber 1900, the substrate 1604 is positioned upon the substrate support 1908. The substrate support 1908 incorporates a suitable substrate chucking mechanism (e.g., electrostatic, mechanical clamping, or the like) for holding the substrate 1604. The reactor top 1928 incorporates a quartz dielectric window 1976, which allows the transmission of energy from the antenna 1902 into the chamber. The dielectric window 1976, the substrate support 1908, and anodized aluminum chamber walls 1952 define the confined plasma volume. Gas is supplied to the confined plasma volume by the gas source 1910 and is exhausted from the confined plasma volume through an exhaust port by the exhaust pump 1920. A first RF source 1944 is electrically connected to the antenna. A second RF source 1948 is electrically connected to the substrate support 1908. In this example, the first RF source 1944 provides a signal with a 13.56 MHz frequency, and the second RF source 1948 provides a signal with a 13.56 MHz frequency.

During the deposition of the deposition layer (step 1702), a pressure of 140 mTorr is provided to the chamber. The RF source provides 400 Watts of power at 27 MHz of plasma frequency. The gas flow is a combination of CH₃F and N₂, with CH₃F at 150 sccm and N₂ at 75 sccm.

During the anisotropic etch of the deposition layer (step 1704), a pressure of 40 mTorr is provided to the chamber. The first RF source 1994 provides 800 Watts of power at 27 MHz of plasma frequency by the antenna 1902 to the plasma volume 1940. A bias of -175 volts is applied to the substrate support to accelerate positive ions to the substrate to facilitate etching. The etch gas source 1916 provides 75 sccm of CF₄.

The anisotropic etch of the conductive layer (step 1708) is accomplished using four etches a BT (breakthrough) etch, an ME1 (main etch 1), ME2 (main etch 2), and an OE (over etch). For the BT a 40 mTorr pressure is provided. 800 Watts of power at 27 MHz of plasma frequency are provided through the antenna 1902 to the chamber 1900. A bias of -175 volts is applied to the substrate support 1908 to accelerate ions to the substrate to facilitate etching. The etch source provide 75 sccm of CF₄ for about 10 seconds.

For the ME1 a 10 mTorr pressure is provided. 800 Watts are provided through the antenna 1902 to the chamber 1900. A bias of -90 volts is applied to the substrate support 1908 to accelerate ions to the substrate to facilitate etching. The etch source provide 100 sccm of Cl₂, 100 sccm HBr, and 5 sccm O₂ for about 45 seconds.

For the ME2 a 20 mTorr pressure is provided. 400 Watts are provided through the antenna 1902 to the chamber 1900. A bias of -170 volts is applied to the substrate support 1908 to accelerate ions to the substrate to facilitate etching. The etch source provide 20 sccm of Cl₂, 360 sccm HBr, and 5 sccm O₂. An endpoint detection is used to determine when to stop this etch.

For the OE a 60 mTorr pressure is provided. 500 Watts are provided through the antenna 1902 to the chamber 1900. A bias of -210 volts is applied to the substrate support 1908 to accelerate ions to the substrate to facilitate etching. The etch source provide 267 sccm of He, 133 sccm HBr, and 2 sccm O₂ for about 80 seconds.

While other materials, such as hydrocarbon-included polymer, may be used to form the deposition layer, these materials cause more PR wiggling and striation than fluorine-included polymer deposition. Therefore, it is more preferable to use fluorine-included polymer to form the deposition layer.

Other embodiments may use a hardmask for the mask. In such embodiments, a photoresist mask may be used to open a hardmask. The deposition layer may be placed over the hardmask to reduce the spacing. In the alternative, the deposition layer may be placed over the photoresist before etching the hardmask.

While this invention has been described in terms of several preferred embodiments, there are alterations, permutations, and various substitute equivalents, which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, permutations, and various substitute equivalents as fall within the true spirit and scope of the present invention.

What is claimed is:

1. A method for forming a feature in a layer, comprising:
 - forming a photoresist layer over the layer;
 - patterning the photoresist layer to form photoresist features with photoresist sidewalls, where the photoresist features have a first critical dimension;
 - depositing a fluorine-containing conformal layer over the sidewalls of the photoresist features to reduce the critical dimensions of the photoresist features;
 - defluorinating the fluorine-containing conformal layer; and
 - etching features into the layer, wherein the layer features have a second critical dimension, which is less than the first critical dimension.
2. The method, as recited in claim 1, wherein the depositing the conformal layer over the sidewalls of the photoresist features, comprises:
 - a first deposition with a first gas chemistry to form a first deposition plasma; and
 - a second deposition with a second gas chemistry to form a second deposition plasma, wherein the first gas chemistry is different than the second gas chemistry.
3. The method, as recited in claim 2, wherein the fluorine-containing conformal layer is formed using fluorine-included polymer.

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4. The method, as recited in claim 3, wherein deflourinating removes the fluorine and leaves the polymer.

5. The method, as recited in claim 3, wherein the depositing the conformal layer over the photoresist features further comprises:

a third deposition with the first gas chemistry to form a third deposition plasma; and

a fourth deposition with the second gas chemistry to form a fourth deposition plasma.

6. The method, as recited in claim 5, wherein the second critical dimension is not greater than 70% of the first critical dimension.

7. The method, as recited in claim 6, wherein the depositing the conformal layer over the sidewalls forms substantially vertical sidewalls.

8. The method, as recited in claim 7, wherein the photoresist layer is formed from at least one selected from the group consisting of 248 nm photoresist or 193 nm photoresist and the feature has a CD not greater than 140 nm.

9. The method, as recited in claim 7, further comprising stripping the photoresist layer and deposited conformal layer with a single stripping step.

10. The method, as recited in claim 9, wherein the stripping the photoresist layer and deposited conformal layer comprises ashing the photoresist layer and deposited layer.

11. The method, as recited in claim 6, wherein the conformal layer has a sidewall thickness, wherein the conformal layer has substantially the same sidewall thickness from a top to a bottom of the feature.

12. The method, as recited in claim 6, wherein the conformal layer has a sidewall thickness and a photoresist feature bottom thickness, wherein the sidewall thickness is greater than the photoresist feature bottom thickness.

13. The method, as recited in claim 2, wherein the fluorine is removed from the conformal layer by applying a third gas chemistry to the conformal layer.

14. The method, as recited in claim 13, wherein the third gas chemistry comprises nitrogen (N₂) and oxygen (O₂).

15. The method, as recited in claim 14, wherein the ratio of nitrogen and oxygen ranges from two-part nitrogen to one-part oxygen to one-part nitrogen to ten-party oxygen.

16. A semiconductor device formed by the method of claim 1.

17. A method for forming a feature in a layer, comprising: forming a photoresist layer over the layer;

patterning the photoresist layer to form photoresist features with photoresist sidewalls, where the photoresist features have a first critical dimension;

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depositing a fluorine-containing layer over the sidewalls of the photoresist features to reduce the critical dimensions of the photoresist features, wherein the depositing the layer over the sidewalls of the photoresist feature, comprises:

a first deposition with a first gas chemistry to form a first deposition plasma; and

a second deposition with a second gas chemistry to form a second deposition plasma, wherein the first gas chemistry is different than the second gas chemistry;

deflourinating the fluorine-containing layer; and

etching features into the layer, wherein the layer features have a second critical dimension, wherein the second critical dimension is not greater than 70% of the first critical dimension.

18. The method, as recited in claim 17, wherein the second critical dimension is not greater than 60% of the first critical dimension.

19. The method, as recited in claim 17, wherein the fluorine-containing layer is formed using fluorine-included polymer.

20. The method, as recited in claim 19, wherein deflourinating removes the fluorine and leaves the polymer.

21. The method, as recited in claim 19, wherein the depositing the layer over the photoresist features further comprises:

a third deposition with the first gas chemistry to form a third deposition plasma; and

a fourth deposition with the second gas chemistry to form a fourth deposition plasma.

22. The method, as recited in claim 21, wherein the depositing the layer over the sidewalls forms substantially vertical sidewalls.

23. The method, as recited in claim 17, wherein the fluorine is removed from the layer by applying a third gas chemistry to the conformal layer.

24. The method, as recited in claim 23, wherein the third gas chemistry comprises nitrogen (N₂) and oxygen (O₂).

25. The method, as recited in claim 24, wherein the ratio of nitrogen and oxygen ranges from two-part nitrogen to one-part oxygen to one-part nitrogen to ten-party oxygen.

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